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XCIX.—ON THE OXIMES OF MUCOPHENOXYCHLORIC AND MUCOPHENOXYBROMIC ACIDS.

BY JOHN A. WIDTSOE.

C.—ON THE ACTION OF ALUMINIC CHLORIDE AND BENZOL UPON MUCOCHLORYL CHLORIDE, MUCOBROMYL BROMIDE, AND THE CORRESPONDING ACIDS.

BY FREDERICK L. DUNLAP.

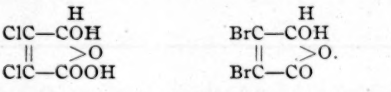
INTRODUCTION.

BY HENRY B. HILL.

Several years ago Hill and Cornelison[1] found that mucochloric and mucobromic acids yielded with hydroxylamine oximes of perfectly normal character, while the bromanhydrides of these acids could easily be converted, by reduction, into the corresponding substituted crotonolactones. The formation of oximes indicated that the acids in question contained the aldehyde group, and that their structure corresponded to the formulæ

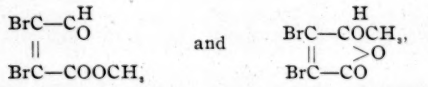
[1] This JOURNAL, **16**, 188, 277; Proc. Amer. Acad., **29**, 1.

while the ready reduction of the bromanhydrides to crotonolactones showed with equal probability that the formulæ of these acids were



These two acids, therefore, showed, like the orthoaldehyde acids of the aromatic series investigated by Lieberman, Allendorf, Racine, Perkin, and others, the behavior ordinarily described by the term tautomerism.

Hill and Cornelison suggested the possibility of discriminating between the two forms for the methyl ester of mucobromic acid,

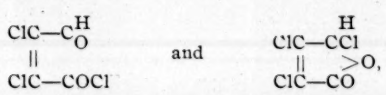


in that the first form would probably react with hydroxylamine as readily as the free acid, while the second form would yield with more difficulty a derivative of the ordinary aldoxime. The experiments which they made, with mucobromic and mucochloric acids, and with their methyl esters showed that while the reaction with the free acids was completed in a very short time, little or no product could be obtained from the esters even on long standing. It seemed desirable to determine whether other acids of this series would show the same difference in behavior when compared with their esters, and Mr. J. A. Widtsoe, therefore, undertook the study of mucophenoxybromic and mucophenoxychloric acids in this direction. Hill and Cornelison had reduced the bromanhydrides of these acids to the corresponding lactones,

and had prepared also their oximes; but they had made no study of their esters. In the course of his investigations Mr. Widtsoe showed that the methyl esters of these acids reacted

promptly with hydroxylamine, and gave at once bodies which were identical with the esters made from the oximes through the action of methyl iodide upon their silver salts. The marked differences in behavior which had been shown by mucobromic or mucochloric acid and their methyl esters, disappeared as soon as one atom of halogen was replaced by the phenoxy group. It is not easy to account for this radical change in behavior, but in any case the prompt reaction with hydroxylamine is to be taken as evidence that these esters contain the aldehyde group. Mr. Widtsoe also made a more extended study of the oximes in question and their derivatives.

Although the conversion of mucobromic and mucochloric acids through their bromanhydrides into substituted crotonolactones, found its most simple explanation in the assumption that these acids were themselves oxylactones, in view of the general interest attaching to the question of the structure of the δ-aldehyde and δ-ketone acids, it seemed desirable to secure further experimental evidence through reactions of an entirely different character. It is well known that acid chloranhydrides of normal form yield, when treated according to the method of Friedel and Crafts, with aluminic chloride and benzol ketones by the replacement of the chlorine of chloranhydride by the phenyl group. It seemed possible that this reaction might give the means of distinguishing between the two structural forms

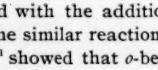


since the first body should give an aldehyde phenylketone, while the second should yield a dichlordiphenylcrotonic acid. In the same way mucochloric acid itself, when treated with benzol and aluminic chloride, might also yield dichlordiphenylcrotonic acid, if it is an oxylactone, while an aldehyde acid of ordinary form could hardly give such a product.

Mr. F. L. Dunlap undertook the experimental investigation of these reactions, and found that dichlordiphenylcrotonic acid could be formed with satisfactory yield when muco-

chloryl chloride or mucochloric acid was heated in benzol solution with aluminic chloride; with mucobromic acid the analogous dibromdiphenylcrotonic acid was formed. The constitution of these acids was determined with precision by their conversion through oxidation into diphenylacetic acid.

These results apparently warrant the conclusion that mucochloric acid and its chloranhydride have the lactone structure. If the aldehyde formula is adopted the formation of the dichlorphenylcrotonic acid in either case can be explained only by the assumption that the aldehyde group is first attacked with the addition of benzol. As far as I am aware, but one similar reaction has been observed. In 1881, v. Pechmann[1] showed that *o*-benzoylbenzoic acid could be converted into phthalophenone by the action of aluminic chloride and benzol; a better yield was obtained in the same way from *o*-benzoylbenzoic acetic anhydride. While v. Pechmann notes that the latter reaction is anomalous in that acid anhydrides were shown by Friedel and Crafts to yield ketones, he remarks that the difference is due to the great reactive-power of the ketone group of the benzoylbenzoic acid. The conclusion could quite as fairly be drawn, however, from v. Pechmann's observations, that the benzoylbenzoic acid and its anhydride with acetic acid had the structure



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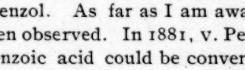
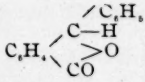


The reaction then becomes perfectly normal. It should be noted in this connection that, according to the observations of Gresly,[2] the anhydride of *o*-benzhydrylbenzoic acid, phenylphthalid,



by the action of aluminic chloride and benzol is converted into triphenylmethanecarboxylic acid, although the reaction with phthalic anhydride apparently ends with the formation of phthalophenone.

[1] Ber. d. chem. Ges., **14**, 1865. [2] Ann. chem. (Liebig), **234**, 241.

THE OXIMES OF MUCOPHENOXYBROMIC AND MUCOPHENOXYCHLORIC ACIDS.[1]

By John A. Widtsoe.

Mucophenoxybromic Acid.

Mucophenoxybromoxime was first made by Hill and Cornelison,[2] and their method has been followed in the preparation of the material needed for this work. It has been found advantageous, however, to diminish the amount of the solvent which they recommend. Instead of dissolving the mucophenoxybromic acid in twenty times its weight of 50 per cent. methyl alcohol, a better yield was obtained when 2 cc. of methyl alcohol of this strength was used for each gram of the acid. Under these conditions the yield was nearly quantitative.

Silver Salt of Mucophenoxybromoxime, $C_4H_3(OC_4H_3)BrNO_3Ag$.—This salt was thrown down as an amorphous, voluminous precipitate when argentic nitrate was added to a neutral solution of the oxime in pure potassic hydrate. It may also be prepared by mixing alcoholic solutions of argentic nitrate and mucophenoxybromoxime, but, as it is somewhat soluble in alcohol, the yield is not satisfactory.

I. 0.3011 gram salt gave with HBr 0.1453 gram AgBr.

II. 0.2886 gram salt gave when heated with HNO_3 0.1381 gram AgBr.

	Calculated for $C_4H_3(OC_4H_3)BrNO_3Ag$.	Found. I.	Found. II.
Ag	27.48	27.72	....
Br	20.35	....	20.36

Methyl Ester of Mucophenoxybromoxime, $C_4H_3(OC_4H_3)BrNO_3CH_3$.—This body could not be made from the oxime by the action of methyl alcohol; the oxime remained unaltered, was converted into its anhydride or the corresponding imide according to the conditions employed. The methyl ester could be prepared, however, by the action of methyl iodide upon the silver salt of mucophenoxybromoxime. The best yield was obtained when the silver salt and methyl iodide

[1] The work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University, in May, 1894, by John A. Widtsoe, then candidate for the degree of Bachelor of Science.

[2] This Journal, **16**, 306; Proc. Amer. Acad., **29**, 53.

were heated with a return-condenser for about an hour. The ester was then taken up with ether, and the residue left by the evaporation of the ethereal solution recrystallized from benzol.

I. 0.2156 gram substance gave 0.3472 gram CO_2 and 0.0586 gram H_2O.

II. 0.2446 gram substance gave 0.1506 gram AgBr.

III. 0.2646 gram substance gave 10.4 cc. moist nitrogen at 19° and under a pressure of 778 mm.

	Calculated for $C_4H_3(OC_4H_3)BrNO_3CH_3$.	Found. I.	II.	III.
C	44.00	43.93	....	....
H	3.33	3.02	....	....
Br	26.67	....	26.20	....
N	4.67	....	....	4.62

The methyl ester of the mucophenoxybromoxime is insoluble in water, carbonic disulphide, or ligroïn; it is sparingly soluble in ether, methyl alcohol, or chloroform; in hot acetone, glacial acetic acid, benzol, or toluol it dissolves more freely, and from the latter it crystallizes well on cooling. It then melts, when heated in the usual way, from 150°–165°, while the melting-point determined by dipping the capillary tube into the heated bath is approximately 168°–170°. It is saponified by sodic or potassic hydrate, while aqueous ammonic hydrate dissolves it only on long standing. In this case a brown resinous body was obtained which has not been further studied. When the ester is treated with hydrochloric acid in alcoholic solution it gives the mucophenoxybromoxime anhydride, and the anhydride is also slowly formed when the ester is suspended in a mixture of acetic acid and acetic anhydride saturated with hydrochloric acid gas. When the ester is boiled with alcohol, slightly acidified with hydrochloric acid, phenoxybrommaleïnimide is formed. A body in all respects identical with the ester first described is formed when hydroxylamine hydrochlorate acts upon methyl mucophenoxybromate in alcoholic solution.

Methyl Mucophenoxybromate, $C_3H(OC_4H_3)BrO_3CH_3$.—Argentic mucophenoxybromate is easily made by adding argentic nitrate to a solution of the potassium salt. The well-dried

salt reacts at ordinary temperatures with methyl iodide with the evolution of heat. The ester thus formed was extracted with ether and recrystallized from ligroïn.

I. 0.2562 gram substance gave 0.4306 gram CO_2 and 0.0749 gram H_2O.

II. 0.2454 gram substance gave 0.1640 gram AgBr.

	Calculated for $C_4H(OC_4H_3)BrO_3CH_3$.	Found. I.	II.
C	46.33	45.86	....
H	3.13	3.25	....
Br	28.07	....	28.44

Methyl mucophenoxybromate forms radiating needles, which melt at 75°–76°. It is readily soluble in alcohol, ether, chloroform, carbonic disulphide, benzol, toluol, or glacial acetic acid. It is sparingly soluble in cold ligroïn, but dissolves more freely on heating, and crystallizes well as the solution cools. It is quickly decomposed when exposed to direct sunlight, and even in diffused light it decomposes when exposed to the air for a few weeks; in a tightly stoppered bottle it softens and turns yellow in the course of a few months.

Hydroxylamine Hydrochlorate with Methyl Mucophenoxybromate.—When a little more than the calculated amount of hydroxylamine hydrochlorate in aqueous solution is added to an alcoholic solution of methyl mucophenoxybromate, the oxime ester is immediately thrown down. The substance thus precipitated, when recrystallized from benzol, gave the following results:

I. 0.2743 gram substance gave 0.4444 gram CO_2 and 0.0743 gram H_2O.

II. 0.2224 gram substance gave 0.1364 gram AgBr.

III. 0.3071 gram substance gave 12.6 cc. moist nitrogen at 21° and under a pressure of 762 mm.

	Calculated for $C_4H_3(OC_4H_3)BrNO_3CH_3$.	Found. I.	II.	III.
C	44.00	44.18	....	....
H	3.33	3.01	....	....
Br	26.67	....	26.10	....
N	4.67	....	....	4.68

The physical properties of this substance agree in every respect with those of the ester made from the silver salt of the mucophenoxybromoxime by the action of methyl iodide. When slowly heated it melted as low as 150°, but by more rapid heating the melting-point could be raised to 165°. By dipping the capillary tube into the heated bath its melting-point was found to be approximately 168°–170°.

Ethyl Ester of Mucophenoxybromoxime, $C_4H_2(OC_6H_5)BrNO_3C_2H_5$.—Although the methyl ester could not be formed by the action of methyl alcohol upon the mucophenoxybromoxime, if the oxime was heated for a short time with absolute alcohol, to which a small amount of hydrochloric acid had been added, the ethyl ester was formed without difficulty. The same body was also formed by the action of ethyl iodide upon the silver salt of the oxime. At the boiling-point of the ethyl iodide the reaction is soon complete, and the product may be extracted with ether.

I. 0.2112 gram substance prepared from the silver salt gave 0.3568 gram CO_2 and 0.0684 gram H_2O.

II. 0.2177 gram substance prepared from the silver salt gave 0.1302 gram AgBr.

III. 0.2556 gram substance prepared from the oxime with alcohol gave 0.1533 gram AgBr.

	Calculated for $C_4H_2(OC_6H_5)BrNO_3C_2H_5$.	Found. I.	II.	III.
C	45.87	46.06	....	....
H	3.82	3.60	....	....
Br	25.48	....	25.45	25.53

The ethyl ester of mucophenoxybromoxime is readily soluble in alcohol; more sparingly soluble in chloroform, benzol, toluol, or glacial acetic acetic acid; it is very sparingly soluble even in boiling ligroïn. It crystallizes from water or dilute alcohol in beautiful flat, silky needles, which melt rather sharply at 122°–124°.

Mucophenoxybromoxime Anhydride, $C_4H(OC_6H_5)BrNO_3$.—When hydrochloric acid gas is passed into a concentrated solution of mucophenoxybromoxime in methyl or ethyl alcohol, and the temperature of the liquid is not allowed to rise above 20°, a crystalline precipitate of oxime anhydride is

formed in the course of a few minutes; more of the anhydride may be obtained from the filtrate by the immediate addition of water. The same body may be obtained in pure condition by passing gaseous hydrochloric acid into a solution of oxime in glacial acetic acid, to which about ten per cent. of acetic anhydride has been added. After the solution has stood over night, water throws down the anhydride nearly pure. For analysis it was recrystallized from benzol.

I. 0.2528 gram substance gave 0.4165 gram CO_2 and 0.0556 gram H_2O.

II. 0.2246 gram substance gave 0.1573 gram AgBr.

III. 0.2149 gram substance gave 0.1521 gram AgBr.

IV. 0.2460 gram substance gave 12 cc. moist nitrogen at 20° and under a pressure of 753 mm.

	Calculated for $C_4H(OC_4H_3)BrNO_3$.	Found. I.	II.	III.	IV.
C	44.78	44.92	....	....	....
H	2.24	2.44	....	....	....
Br	29.85	....	29.81	30.12	....
N	5.22	....	....	....	5.53

Mucophenoxybromoxime anhydride is insoluble in water, sparingly soluble in chloroform or carbonic disulphide, readily soluble in methyl alcohol or glacial acetic acid; from benzol it crystallizes in pearly white scales. When heated in ordinary fashion the body melts at 121°, but on rapid heating the melting-point is 124°–126°. It dissolves slowly in a dilute solution of sodic hydrate, and the immediate addition of acid throws down a small quantity of a body melting at 140°–144°, which is without doubt the phenoxybrommaleïnimide. From the solution may then be extracted, by ether, a colorless acid, which, after sublimation, melted at 90°–91°, the melting-point of phenoxybrommaleic anhydride.

Phenoxybrommaleïnimide, $C_4H(OC_4H_3)BrNO_2$.—Although most of the oximes of similar structure can be converted by heat through their anhydrides into the imides, the phenoxybrommaleïnimide apparently cannot be made in this way. If mucophenoxybromoxime anhydride is suspended in a small amount of methyl or ethyl alcohol saturated with gaseous hydrochloric acid it slowly goes into solution, and the addi-

tion of water to this solution then precipitates phenoxybrommaleïnimide. The oxime may also be converted into the imide by heating its alcoholic solution for several hours at 100°, or by boiling for some time its solution in methyl alcohol after the addition of a few drops of concentrated hydrochloric acid. By following the last method the imide is obtained, combined with one molecule of methyl alcohol. The substance was recrystallized from benzol for analysis.

I. 0.3174 gram substance gave 0.5244 gram CO_2 and 0.0634 gram H_2O.

II. 0.1992 gram substance gave 0.1372 gram AgBr.

III. 0.1579 gram substance gave 0.1089 gram AgBr.

IV. 0.2861 gram substance gave 0.1971 gram AgBr.

V. 0.2098 gram substance gave 9.3 cc. moist nitrogen at 19° and under a pressure of 765 mm.

	Calculated for $C_4H(OC_4H_3)BrNO_2$.	Found. I.	II.	III.	IV.	V.
C	44.78	45.04	....	....	....	....
H	2.24	2.22	....	....	....	....
Br	29.85	....	29.31	29.36	29.32	....
N	5.23	....	....	....	....	5.13

The phenoxybrommaleïnimide crystallizes in large, colorless plates, which melt at 144°–145° when heated at ordinary speed; by dipping the capillary tube into the heated bath the melting-point was found to be 148°–150°. The crude product always has a faint pink color, which cannot be removed by recrystallization from benzol, but which disappears after several recrystallizations from boiling water. The imide dissolves readily in acetone or glacial acetic acid; it is sparingly soluble in chloroform, and nearly insoluble in ligroïn or carbonic disulphide. It dissolves readily in dilute solutions of the alkaline hydrates, and the immediate addition of acid reprecipitates it in part unchanged. After the lapse of a short time the alkaline solution contains phenoxybrommaleïc acid, which was identified by the melting-point 90°–91° of the sublimed anhydride. When the imide is boiled for several hours with water the same change takes place.

It has already been mentioned that when the phenoxybrommaleïnimide is prepared by boiling the oxime with

methyl alcohol, to which a few drops of hydrochloric acid are added, the imide thrown down with water contains one molecule of methyl alcohol. The same product can be made by boiling the imide with methyl alcohol and hydrochloric acid. The body crystallizes from benzol in long, coarse needles, which lose their crystal alcohol readily at 100°. When dissolved in hot water the compound is also immediately broken up, and the ordinary imide crystallizes out as the solution cools.

I. 0.3148 gram substance gave 0.5076 gram CO_2 and 0.0963 gram H_2O.

II. 0.2233 gram substance gave 0.1372 gram AgBr.

III. 0.2019 gram substance gave 0.1267 gram AgBr.

IV. 0.2472 gram substance gave 10.0 cc. moist nitrogen at 20° and under a pressure of 752 mm.

V. 0.1651 gram substance lost at 90°–100° 0.0172 gram.

	Calculated for $C_4H(OC_6H_5)BrNO_2.CH_3OH$.	Found. I.	II.	III.	IV.	V.
C	44.00	43.97	....	....	....	....
H	3.33	3.40	....	....	....	....
Br	26.67	....	26.14	26.71	....	....
N	4.67	....	....	....	4.58	....
CH_3OH	10.67	....	....	....	....	10.42

Silver Salt of Phenoxybrommaleïnimide, $C_4(OC_6H_5)BrNO_2Ag$. —When alcoholic solutions of phenoxybrommaleïnimide and argentic nitrate are mixed together no reaction takes place even after the lapse of many hours. The addition of alcoholic ammonia, however, immediately throws down small, yellowish, granular crystals of the silver salt of the imide.

I. 0.2341 gram substance, when heated with nitric acid, gave 0.1183 gram AgBr.

II. 0.2477 gram substance, precipitated with hydrobromic acid, gave 0.1230 gram AgBr.

	Calculated for $C_4(OC_6H_5)BrNO_2Ag$.	Found. I.	II.
Br	21.34	21.51	....
Ag	28.80	....	28.52

Mucophenoxychloric Acid.

Methyl Ester of Mucophenoxychloroxime, $C_4H_3(OC_6H_5)ClNO_3$

CH_3.—The ester could not be made directly from the oxime by the action of methyl alcohol; it could be made, however, by the action of methyl iodide upon the silver salt of the oxime. The reaction was soon finished at 40°; the ester was then extracted with ether and recrystallized from benzol.

I. 0.2383 gram substance gave 0.4509 gram CO_2 and 0.0770 gram H_2O.

II. 0.2599 gram substance gave 0.1444 gram AgCl.

III. 0.2752 gram substance gave 13.3 cc. moist nitrogen at 23° and under a pressure of 749 mm.

	Calculated for $C_4H_3(OC_6H_5)ClNO_3CH_3$.	Found. I.	II.	III.
C	51.66	51.60	....	....
H	3.91	3.59	....	....
Cl	13.90	....	13.74	....
N	5.48	....	....	5.36

The methyl ester of the mucophenoxychloroxime forms long, silky needles, which are insoluble in water, sparingly soluble in carbonic disulphide or cold chloroform. The body dissolves freely in hot benzol or toluol, and crystallizes well on cooling. The melting-point varies with the rate of heating; when heated in the ordinary way it melts at 156°–160°, but on dipping the substance into the heated bath its melting-point seems to be 162°–166°. This ester may also be made by the action of hydroxylamine hydrochlorate upon methyl mucophenoxychlorate.

Methyl Mucophenoxychlorate, $C_4H(OC_6H_5)ClO_3CH_3$.—Methyl iodide reacts upon dry argentic mucophenoxychlorate with the evolution of heat. The methyl ester thus formed may be extracted by ether and recrystallized from ligroïn.

I. 0.1947 gram substance gave 0.3903 gram CO_2 and 0.0622 gram H_2O.

II. 0.2560 gram substance gave 0.1531 gram AgCl.

	Calculated for $C_4H(OC_6H_5)ClO_3CH_3$.	Found. I.	II.
C	54.89	54.67	....
H	3.74	3.55	....
Cl	14.76	....	14.79

Methyl mucophenoxychlorate is soluble in most of the ordi-

nary organic solvents. From its solution in boiling ligroïn it crystallizes on cooling in clusters of radiating needles, which melt at 59°. Like the corresponding body containing bromine, it decomposes on standing.

Hydroxylamine Hydrochlorate with Methyl Mucophenoxychlorate.—When an aqueous solution containing somewhat more than the theoretical amount of hydroxylamine hydrochlorate is added to an alcoholic solution of methyl mucophenoxychlorate, the oxime of the ester is immediately thrown down. This body was in appearance and behavior identical with the ester already described as made by the action of methyl iodide upon the silver salt of the mucophenoxychloroxime. When recrystallized from benzol it also contained the proper percentage of chlorine.

0.2068 gram substance gave 0.1161 gram AgCl.

	Calculated for $C_4H_3(OC_4H_3)ClNO_3CH_3$.	Found.
Cl	13.90	13.88

Mucophenoxychloroxime Anhydride, $C_4H(OC_4H)ClNO_3$.—When gaseous hydrochloric acid is passed into a well-cooled solution of mucophenoxychloroxime in six or seven times its weight of methyl alcohol the solution remains clear; but, if the action is not too long continued, water throws down a voluminous precipitate of the anhydride. The same body may also be made by dissolving the oxime in glacial acetic acid mixed with 10 per cent. of acetic anhydride and saturated with hydrochloric acid gas. The mixture is allowed to stand for twenty-four hours and the anhydride then precipitated by the addition of water. For analysis the substance was recrystallized from carbonic disulphide.

I. 0.2793 gram substance gave 0.5522 gram CO_2 and 0.0621 gram H_2O.

II. 0.2111 gram substance gave 0.1362 gram AgCl.

III. 0.2781 gram substance gave 14.9 cc. moist nitrogen at 21° and under a pressure of 776 mm.

	Calculated for $C_4H(OC_4H_3)ClNO_3$.	Found. I.	II.	III.
C	53.69	53.92	....	....
H	2.68	2.47	....	....
Cl	15.88	....	15.95	....
N	6.26	....	....	6.23

Mucophenoxychloroxime anhydride is readily soluble in chloroform, benzol, toluol, or glacial acetic acid; it is sparingly soluble in carbonic disulphide, and from the hot solution it is deposited in large, flexible, pearly scales, which melt rather sharply at 96°–98°. It dissolves sparingly in boiling water, and phenoxychlormaleïnimide is deposited as the solution cools; it also dissolves slowly in dilute solutions of the alkaline hydrates.

Phenoxychlormaleïnimide, $C_4H(OC_6H_5)ClNO_2$.—Mucophenoxychloroxime anhydride slowly isomerizes in strongly acid alcoholic solution and forms the corresponding phenoxychlormaleïnimide. The imide is also formed when an alcoholic solution of the oxime is heated for several hours at 100° in a sealed tube. It may, perhaps, most conveniently be prepared by saturating a concentrated alcoholic solution of the oxime with hydrochloric acid gas and allowing the solution to stand for a day or two. For analysis the substance was recrystallized from water.

I. 0.2618 gram substance gave 0.5152 gram CO_2 and 0.0567 gram H_2O.

II. 0.1886 gram substance gave 0.1202 gram AgCl.

III. 0.2257 gram substance gave 12.4 cc. moist nitrogen at 24° and under a pressure of 756 mm.

	Calculated for $C_4H(OC_6H_5)ClNO_2$.	Found. I.	II.	III.
C	53.69	53.68	....	....
H	2.68	2.41	....	....
Cl	15.88	....	15.75	....
N	6.26	....	....	6.12

Phenoxychlormaleïnimide is readily soluble in alcohol, ether, chloroform, benzol, toluol, or glacial acetic acid, but is sparingly soluble in carbonic disulphide, and almost insoluble in ligroïn. It is sparingly soluble in cold water, more freely soluble in hot water, and, as the solution cools, it separates in clustered, flattened needles, which melt at 118°–119°. On long boiling with water it is converted into the acid ammonium salt of phenoxychlormaleïc acid. Sawyer[1] gives the melting-point of the anhydride of this acid as 97°, while the

[1] Proc. Amer. Acad., **29**, 248.

sublimed acid obtained from this imide melted at 94°–95°. The imide dissolves readily in dilute sodic hydrate, and is reprecipitated from solutions, not too dilute, by the immediate addition of acid. An alcoholic solution throws down a yellowish, granular precipitate on the addition of alcoholic solutions of argentic nitrate and ammonia. Phenoxychlormaleïnimide also combines with methyl alcohol to form a compound analogous to that formed in the same way from phenoxybrommaleïnimide.

ON THE ACTION OF ALUMINIC CHLORIDE AND BENZOL UPON MUCOCHLORYL CHLORIDE, MUCOBROMYL BROMIDE, AND THE CORRESPONDING ACIDS.[1]

BY FREDERICK L. DUNLAP.

Mucochloric Acid.

The mucochloric acid needed for this work was made by the action of manganic dioxide and hydrochloric acid upon pyromucic according to a slight modification of the method already described from this laboratory.[2] Instead of adding the manganic dioxide in calculated amount to the pyromucic acid suspended in concentrated hydrochloric acid, the pyromucic acid and manganic dioxide were intimately mixed, and the mixture was then added in four portions, at intervals of ten to fifteen minutes each, to the necessary amount of hydrochloric acid (sp. gr. 1.18). This slight modification in the process increased the yield of mucochloric acid to about 75 per cent. of the weight of pyromucic acid taken.

Mucochloryl Chloride, $C_4HCl_3O_2$.—Mucochloric acid was heated gently with somewhat more than one molecule of phosphoric pentachloride. The product was then shaken with cold water, taken up with ether, and the ethereal solution dried with calcic chloride. On evaporation of the ether a yellowish oil was obtained, which attacked vigorously the mucous membrane of the eyes and nose. This product was used without farther purification in subsequent work, al-

[1] The work described in the following paper formed a part of a thesis presented to the Faculty of Arts and Sciences of Harvard University in May, 1895, by Frederick L. Dunlap, then candidate for the degree of Doctor of Philosophy.

[2] This JOURNAL, **9**, 160; Proc. Amer. Acad., **22**, 327.

though an analysis showed that the percentage of chlorine which it contained was too low.

0.2684 gram substance gave 0.5899 gram AgCl.

	Calculated for $C_4HCl_3O_2$.	Found.
Cl	56.80	54.34

As mucochloryl chloride had not yet been described a portion of this crude product was submitted to fractional distillation under diminished pressure. Under a pressure of 15 mm. a product was obtained which showed the constant boiling-point 100°–101°, and which contained the required percentage of chlorine.

0.2100 gram substance gave 0.4833 AgCl.

	Calculated for $C_4HCl_3O_2$.	Found.
Cl	56.80	56.90

Dichlordiphenylcrotonic Acid, $C_4H_2Cl_2(C_6H_5)_2O_2$.—Mucochloryl chloride was dissolved in four times its weight of benzol, diluted with twice its volume of carbonic disulphide, and anhydrous aluminic chloride was then added to the solution. The evolution of hydrochloric acid was at once noticeable, and for the completion of the reaction it was found necessary to add an amount of aluminic chloride equal to two or three times the weight of mucochloryl chloride taken. In order to accelerate the action, the flask was heated with a return-condenser; exposure to the direct sunlight also appeared to facilitate the reaction. After heating from thirty to forty hours the evolution of hydrochloric acid ceased, and the contents of the flask were then poured into dilute hydrochloric acid. The carbonic disulphide and benzol were driven off by warming the whole upon the water-bath, and the heat was continued until the oily viscous liquid, which was first obtained, solidified. The crystalline product was then boiled with water to remove all unaltered mucochloryl chloride or mucochloric acid, and the dark-colored residue, after thorough drying, extracted with cold benzol. The main product of the reaction is sparingly soluble in cold benzol, while the tarry by-products are to a great extent removed. The substance is finally purified by repeated recrystallization from glacial acetic

acid or from ligroïn. This same body may also be made more conveniently by the action of aluminic chloride and benzol upon mucochloric acid itself. The method of preparation and purification is identical with that just described, except that but half of the amount of aluminic chloride given above is needed to complete the reaction.

I. 0.1991 gram substance made from mucochloryl chloride gave 0.4596 gram CO_2 and 0.0730 gram H_2O.

II. 0.1887 gram substance made from mucochloryl chloride gave 0.1769 gram AgCl.

III. 0.2261 gram substance made from mucochloric acid gave 0.2125 gram AgCl.

	Calculated for $C_{10}H_{12}Cl_2O_3$.	Found. I.	II.	III.
C	62.55	62.95	....	....
H	3.91	4.07	....	....
Cl	23.13	....	23.17	23.24

Dichlordiphenylcrotonic acid is insoluble in water, readily soluble in ether or acetone, somewhat more sparingly soluble in alcohol or chloroform; it is sparingly soluble in cold benzol or carbonic disulphide, although it dissolves more freely on heating. From boiling ligroïn it crystallizes in short, colorless, frequently clustered prisms, which melt at 152°. It dissolves readily in solutions of the alkalies in the cold, and these solutions yield with acids a viscous precipitate, which solidifies on standing. If the alkaline solution is heated, decomposition ensues, and a colorless oil separates. The methyl and ethyl esters of this acid appear to be liquids, but for its better characterization several of its salts were made.

Baric Dichlordiphenylcrotonate, $Ba(C_{10}H_{11}Cl_2O_3)_2.2H_2O$.—Baric chloride added to an ammoniacal solution immediately throws down the barium salt in the form of clusters of minute radiating needles. The salt is so sparingly soluble even in boiling water that it was well washed and analyzed without recrystallization.

I. 0.2346 gram air-dried salt gave 0.0686 gram $BaSO_4$.

II. 0.5250 gram air-dried salt lost at 110° 0.0234 gram H_2O.

	Calculated for $Ba(C_{10}H_{11}Cl_2O_3)_2.2H_2O$.	Found. I.	II.
Ba	17.45	17.19	....
H_2O	4.59	....	4.46

0.2222 gram anhydrous salt gave 0.0690 gram $BaSO_4$.

	Calculated for $Ba(C_{18}H_{11}Cl_2O_3)_2$.	Found.
Ba	18.29	18.25

Calcic Dichlordiphenylcrotonate, $Ca(C_{18}H_{11}Cl_2O_3)_2.2H_2O$.— This salt was made by precipitating an ammoniacal solution of the acid with calcic chloride. The microcrystalline precipitate was almost insoluble in water and was analyzed without further purification.

I. 0.1921 gram air-dried salt gave 0.0386 gram $CaSO_4$.

II. 0.3244 gram air-dried salt lost at 100° 0.0167 gram H_2O.

	Calculated for $Ca(C_{18}H_{11}Cl_2O_3)_2.2H_2O$.	Found. I.	Found. II.
Ca	5.82	5.91	....
H_2O	5.23	....	5.15

0.1832 gram salt dried at 110° gave 0.0377 gram $CaSO_4$.

	Calculated for $Ca(C_{18}H_{11}Cl_2O_3)_2$.	Found.
Ca	6.14	6.05

Oxidation of Dichlordiphenylcrotonic Acid.

Dichlordiphenylcrotonic acid was readily attacked by potassic permanganate in alkaline solution, and the reaction was studied more in detail in order to establish the structure of the acid. The acid was dissolved in an excess of sodic carbonate in dilute solution, and rather more than two-thirds of a molecule of potassic permanganate was added. The mixture was then allowed to stand at ordinary temperature for several hours until the color had disappeared. On the addition of acid to the filtered solution a yellowish, viscous mass was thrown down, which gradually solidified on standing. This crude oxidation-product, which amounted to about 30 per cent. of the weight of the acid taken, had a distinct odor of benzophenone, and gave with concentrated sulphuric acid the deep-red color described by Zinin[1] as characteristic of benzilic acid. After recrystallization from glacial acetic acid, it no longer gave this color reaction, and analysis showed that it had the percentage composition of diphenylacetic acid.

[1] Ann. Chem. (Liebig), 31, 330.

0.1948 gram substance gave 0.5656 gram CO_2 and 0.1050 gram H_2O.

	Calculated for $C_{14}H_{13}O_3$.	Calculated for $C_{14}H_{12}O_3$.	Found.
C	79.25	73.69	79.18
H	5.66	5.26	5.99

The acid recrystallized from glacial acetic acid melted at 144°–145°, and this melting-point could not be raised by further recrystallization. The melting-point of diphenylacetic acid has been found to be somewhat higher by other observers: Jena[1] gives it as 146°, Symons and Zincke[2] as 145°–146°, while Friedel and Balsohn[3] found it to be 148°. The identity of the acid was definitely established, however, by the melting-point of its ethyl ester, 57°–58°, which agrees precisely with the observations of Symons and Zincke. When warmed with concentrated sulphuric acid it gave the greenish-yellow color described by Jena.

Reduction of Diphenyldichlorcrotonic Acid.

Diphenyldichlorcrotonic acid was dissolved in a dilute solution of sodic carbonate and an excess of a 4 per cent. sodium amalgam was added. After standing over night, the solution was decanted from the mercury and acidified. The viscous acid which separated gradually solidified on standing, and on crystallization from high-boiling ligroïn, it was obtained in clusters of small-pointed, radiating prisms. An analysis of the acid showed that its composition corresponded more nearly to that of a diphenylbutyric than a diphenylcrotonic acid.

0.2382 gram substance gave 0.6996 gram CO_2 and 0.1392 gram H_2O.

	Calculated for $C_{16}H_{14}O_2$.	Calculated for $C_{14}H_{14}O_2$.	Found.
C	80.00	80.67	80.09
H	6.67	5.88	6.49

The behavior of the acid toward bromine farther showed that it was a derivative of butyric and not of crotonic acid; when dissolved in chloroform no addition-product was formed, even after the lapse of several days. The γ-diphenylbutyric

[1] Ann. Chem. (Liebig), **155**, 85. [2] Ann. Chem. (Liebig), **171**, 129.
[3] Bull. Soc. Chim., **33**, 590.

acid is readily soluble in ether, alcohol, benzol, carbonic disulphide, and glacial acetic acid, but is more sparingly soluble in chloroform; it is insoluble in water. When crystallized from ligroïn it melts at 106°.

Argentic γ-Diphenylbutyrate, $AgC_{16}N_{15}O_2$.—The silver salt was made by the addition of argentic nitrate to a neutral solution of the ammonium salt. It appeared to be amorphous, and was practically insoluble in water.

0.2315 gram salt gave 0.0955 gram AgCl.

	Calculated for $AgC_{16}H_{15}O_2$.	Found.
Ag	31.13	31.06

The barium and calcium salts of the acid are amorphous.

Mucobromic Acid.

Many attempts were made to prepare the dibromdiphenylcrotonic acid by the action of aluminic chloride and benzol upon mucobromyl bromide. Although the process was modified in various ways, the product in each case was a black, resinous mass, from which no crystalline body could be isolated. When mucobromic acid, however, was substituted for the mucobromyl bromide, a satisfactory product could be obtained without difficulty.

Dibromdiphenylcrotonic Acid, $C_4H_2Br_2(C_6H_5)_2O_2$.—In preparing this acid essentially the same method was followed that has already been described for making dichlordiphenylcrotonic acid from mucochloric acid. Mucobromic acid was dissolved in five times its weight of benzol, diluted with twice its volume of carbonic disulphide; anhydrous aluminic chloride was then added, and the solution heated with return-condenser. In order to complete the reaction, it was found necessary to add an amount of aluminic chloride equal to one and a half times the weight of the mucobromic acid taken. The dark-colored product which was obtained was purified by washing with small quantities of benzol and recrystallization from glacial acetic acid.

I. 0.1751 gram substance gave 0.3091 gram CO_2 and 0.0512 gram H_2O.

II. 0.1778 gram substance gave 0.1696 gram AgBr.

	Calculated for $C_{14}H_{12}Br_2O_4$.	Found. I.	Found. II.
C	48.49	48.15	....
H	3.03	3.25	....
Br	40.40	....	40.60

Dibromdiphenylcrotonic acid is insoluble in water; readily soluble in alcohol, ether, chloroform, or carbonic disulphide; it is more sparingly soluble in cold benzol or ligroïn, but dissolves freely on heating. From glacial acetic acid it crystallizes in clustered, pointed prisms, which melt at 146°–147.° It is decomposed by heating its alkaline solution, and throws down a colorless oil; but it may be reprecipitated unchanged from cold alkaline solutions. The ethyl ester of the acid was obtained only in the form of a liquid and was not further examined; its methyl ester and several of its salts were made.

Methyl Dibromdiphenylcrotonate, $C_{14}H_{12}Br_2O_2CH_3$. — This body could not conveniently be made by the action of gaseous hydrochloric acid upon a solution of the acid in methyl alcohol. It was prepared without difficulty, however, by heating a solution of the acid in four times its weight of methyl alcohol with the addition of concentrated sulphuric acid. The ester was precipitated with water, taken up with ether, and the ethereal solution dried with calcic chloride after thorough washing with a dilute solution of sodic carbonate. The oily residue left by the ester soon solidified, and the body was then purified by recrystallization from alcohol.

0.1883 gram substance gave 0.1730 gram AgBr.

	Calculated for $C_{14}H_{12}Br_2O_2CH_3$.	Found.
Br	39.02	39.09

Methyl dibromdiphenylcrotonate is readily soluble in ether, chloroform, benzol, or carbonic disulphide, more sparingly soluble in ligroïn. From alcohol it crystallizes in four-sided pyramids, which melt at 79°–80°.

Baric Dibromdiphenylcrotonate, $Ba(C_{14}H_{11}Br_2O_4)_2.3H_2O$.— This salt is thrown down as a microcrystalline precipitate on the addition of baric chloride to an ammoniacal solution of the acid. It is very sparingly soluble even in boiling water; it was, therefore, thoroughly washed and analyzed without

further purification. At temperatures above 100° it was soon decomposed.

I. 0.2075 gram air-dried salt gave 0.0484 gram $BaSO_4$.

II. 0.4575 gram air-dried salt lost at 100° 0.0244 gram H_2O.

	Calculated for $Ba(C_{16}H_{11}Br_2O_2)_2.3H_2O$.	Found. I.	II.
Ba	13.96	13.71	....
H_2O	5.50	....	5.33

0.2247 gram salt dried at 100° gave 0.0558 gram $BaSO_4$.

	Calculated for $Ba(C_{16}H_{11}Br_2O_2)_2$.	Found.
Ba	14.78	14.60

Calcic Dibromdiphenylcrotonate, $Ca(C_{16}H_{11}Br_2O_2)_2.2H_2O$.—Calcic chloride added to an ammoniacal solution of the acid immediately throws down the calcium salt in minute, clustered needles, which are very sparingly soluble even in boiling water.

I. 0.2826 gram air-dried salt gave 0.0430 gram $CaSO_4$.

II. 0.6668 gram air-dried salt lost at 110° 0.0274 gram H_2O.

	Calculated for $Ca(C_{16}H_{11}Br_2O_2)_2.2H_2O$.	Found. I.	II.
Ca	4.62	4.48	....
H_2O	4.16	....	4.11

0.2480 gram salt dried at 100° gave 0.0404 gram $CaSO_4$.

	Calculated for $Ca(C_{16}H_{11}Br_2O_2)_2$.	Found.
Ca	4.82	4.79

Argentic Dibromdiphenylcrotonate, $AgC_{16}H_{11}Br_2O_2$.—The silver salt is amorphous and was made by the addition of argentic nitrate to a neutral solution of the ammonium salt.

0.2321 gram salt gave 0.0871 gram AgBr.

	Calculated for $AgC_{16}H_{11}Br_2O_2$.	Found.
Ag	21.47	21.55

Dibromdiphenyl crotonic acid is oxidized readily by potassic permanganate in alkaline solution, and yields diphenylacetic acid. The acid was not analyzed; but its identity was established by its melting-point 144°–145°, the melting-point

of its ethyl ester 57°–58°, and by the characteristic color reaction with sulphuric acid. In the same way the identity of the acid formed from it by reduction was sufficiently determined by the melting-point 106°, and by comparison with the diphenylbutyric acid made from dichlordiphenylcrotonic acid.

Decomposition of Dibromdiphenylcrotonic Acid in Alkaline Solution.

The decomposition which ensues when dibromdiphenylcrotonic acid, or the corresponding body containing chlorine, is heated in alkaline solution has already been mentioned. While there could be little doubt that the colorless oil which was formed in either case was a substituted diphenylallylene, it seemed worth while to study the reaction farther. Dibromdiphenylcrotonic acid was, therefore, dissolved in a dilute solution of sodic carbonate, and the strongly alkaline solution boiled with reverse-condenser. The liquid soon became turbid with the separation of oil drops and, after the completion of the reaction, the oil was distilled over with steam, taken up with ether, and the ethereal solution dried with calcic chloride. The residue left on evaporation of the ether showed no tendency to crystallize and, as the quantity of material was necessarily limited, it was thought advisable to form at once a bromine addition-product. The oil took up bromine readily with the evolution of heat, and with due care the formation of hydrobromic acid could be prevented. The product then solidified without difficulty, and by recrystallization from ligroïn was obtained in large, clustered, oblique prisms.

0.2115 gram substance gave 0.2753 gram AgBr.

	Calculated for $C_{15}H_{11}Br_3$.	Found.
Br	55.68	55.40

This diphenylbromallylenedibromide is readily soluble in benzol, chloroform, or carbonic disulphide; it dissolves very readily in hot alcohol, but more sparingly in cold. When crystallized from ligroïn the substance melts with decomposition between 120° and 130°. It began to soften when slowly heated at 117°, and melted completely with the evolution of hydrobromic acid at 130°. With concentrated sulphuric acid it gave a dark green color.

CI.—ON CERTAIN DERIVATIVES OF BROMMALEIC AND CHLORMALEIC ACID-ALDEHYDES.

By Henry B. Hill and Eugene T. Allen.

In 1873 Limpricht[1] obtained by the action of aqueous bromine upon pyromucic acid a body to which he gave the formula $C_4H_4O_3$. The isolation of this body was difficult, but material enough was obtained for the necessary analyses. Since it yielded upon oxidation with argentic oxide, an acid which appeared to be fumaric acid, Limpricht concluded that this body was the half aldehyde of fumaric acid. In 1877, v. Baeyer[2] repeated this oxidation with argentic oxide and established the identity of the fumaric acid formed, but he made no attempt to isolate the acid-aldehyde itself. As far as we are aware, no further investigations have been made in this direction, although Limpricht's view of the constitution of the body in question was indirectly confirmed by Hill and Hendrixson,[3] who prepared acetacrylic acid through the same reaction from δ-methylpyromucic acid. Since the few γ-aldehyde-acids which are known are in many respects interesting, it seemed to us worth while to undertake the preparation of larger quantities of this aldehyde-acid of Limpricht, and to make a more thorough study of it.

Although we carefully followed the directions of Limpricht and afterwards modified his method in many different ways, we did not succeed in obtaining the crystalline compound which he described.[4] In every case we obtained a thick, viscous liquid, which did not solidify, even after long standing *in vacuo* over sulphuric acid. This viscous product gave the familiar reactions for aldehydes; it reduced argentic oxide, and even Fehling's solution; it reddened a solution of

[1] Ann. Chem. (Liebig), **168**, 287. [2] Ber. d. chem. Ges., **10**, 1362.

[3] Ber. d. chem. Ges., **23**, 452.

[4] In several cases the hydrobromic acid formed in the reaction was partially neutralized before extracting with ether. When sodic hydrate was used for this purpose, a small quantity of a yellow, pulverulent body was thrown down while the solution was still strongly acid. This substance contained no sodium, and was insoluble in all ordinary neutral solvents; it dissolved in sodic hydrate, and was reprecipitated by the addition of acids. It dissolved also in concentrated sulphuric acid, and separated to all appearance unchanged upon the addition of water. At 185° the substance was decomposed without melting. Lack of material made an extended study of the body impracticable.

rosaniline hydrochlorate decolorized by sulphurous acid, and gave with diazobenzol sulphonate and sodium amalgam, a deep, purple color. Since we were unable to isolate the acid-aldehyde in crystalline form, we attempted to prepare some derivative of it which should be more manageable. Aniline and phenyl hydrazine readily formed insoluble products, but their physical properties did not invite further investigation. With hydroxylamine hydrochlorate, we obtained, although in small quantity, a well-defined crystalline compound, which proved to be the oxime of an acid-aldehyde containing bromine, instead of the derivative of the corresponding unsubstituted acid which we sought. Since the formation of brommaleïc acid-aldehyde had never before been observed, we determined to continue our investigations in this direction. We soon found that the yield of the brommaleïc acid-aldehyde could materially be increased by the addition of more bromine, but we did not succeed in isolating the acid itself.

The oxime was interesting, not only in that it followed the analogy of the oximes of mucobromic and mucochloric acids, and of the orthoaldehyde-acids of the aromatic series, but also in that the corresponding derivatives of succinic acid could be made from it by addition. Furthermore, from the oxime of tribromsuccinic acid-aldehyde, through the loss of carbonic dioxide and hydrobromic acid, could be formed a derivative of acrolein. We also studied briefly the action of chlorine in aqueous solution upon pyromucic acid, and showed that chlormaleïc acid-aldehyde could thus be formed.

Brommaleïc Acid-aldoxime.

The viscous liquids which we had obtained in our attempts to prepare the aldehyde-acid of Limpricht, according to the equation,

$$C_5H_4O_3 + 2Br_2 + 2H_2O = C_4H_4O_3 + CO_2 + 4HBr,$$

were treated with small quantities of cold water, and hydroxylamine hydrochlorate added to the solution. A small amount of a crystalline oxime soon formed, which was collected, dried and purified by precipitation from ethereal solution by the addition of ligroïn. After our analyses had

shown that the body contained bromine, we found that the yield could be increased very considerably by using a third molecule of bromine according to the equation:

$$C_5H_4O_3 + 3Br_2 + 2H_2O = C_4H_3BrO_3 + CO_2 + 5HBr.$$

In this case, however, we found that notable quantities of mucobromic acid were also formed. The pyromucic acid was suspended in about thirty times its weight of cold water, and three molecules of bromine slowly added from a burette with constant cooling and shaking. The first two molecules of bromine are quickly taken up, but the third enters into reaction very slowly, so that three or four days may elapse before the color of the bromine completely disappears. The colorless solution was filtered and thoroughly extracted with ether. The ethereal extract leaves on distillation a viscous residue, which does not differ in appearance from the product obtained by the action of two molecules of bromine, but on extracting this residue with successive portions of cold water, and adding to the solution hydroxylamine hydrochlorate a crude product, amounting to about 40 per cent. of the weight of the pyromucic acid taken, may be obtained. The total weight of aqueous extract should be about five times the weight, that of the hydroxylamine hydrochlorate about one quarter of the weight of pyromucic acid employed. The oxime as it separates is often mixed with more or less mucobromic acid, which under these conditions, does not react as quickly upon the hydroxylamine hydrochlorate as the brommaleïc acid-aldehyde, and sometimes also with mucobromoxime. These two impurities, however, may readily be removed by warming the crude product for a short time with a little water. Mucobromoxime is thus converted into the acid ammonium salt of dibrommaleïc acid, while the small amount of mucobromic acid remains in solution.

I. 0.3120 gram substance gave 0.2878 gram CO_2 and 0.0637 gram H_2O.

II. 0.3133 gram substance gave 0.2891 gram CO_2 and 0.0604 gram H_2O.

III. 0.1238 gram substance gave 0.1201 gram AgBr.

IV. 0.3096 gram substance gave 20.6 cc. moist nitrogen at 25°.2 and under a pressure of 752 mm.

V. 0.1888 gram substance gave 12.5 cc. moist nitrogen at 21° and under a pressure of 767 mm.

	Calculated for $C_4H_4BrNO_3$.	Found. I.	II.	III.	IV.	V.
C	24.74	25.15	25.17	....	....	....
H	2.06	2.27	2.14	....	....	....
Br	41.24	....	....	41.29	....	....
N	7.22	....	....	....	7.33	7.61

Brommaleïc acid-aldoxime crystallizes in small, stout, clustered prisms, with oblique truncations. It dissolves quite readily in alcohol, or in ether; but it is almost insoluble in chloroform, benzol, carbonic disulphide, or ligroïn. It is sparingly soluble in cold water, but dissolves more freely in boiling water; with care it may also be recrystallized from glacial acetic acid. Acetyl chloride does not react upon it. The melting-point varies with the rate at which it is heated. When the temperature is slowly raised, it melts with explosive decomposition at about 143°, but by rapid heating this point may be raised some ten degrees.

The oxime may be boiled for a long time with water without essential alteration, but at 110° in sealed tubes it is soon converted into the acid ammonium salt of brommaleïc acid. This change, although not so readily effected, is identical with that noticed by Hill and Cornelison,[1] and Sawyer,[2] in the case of several oximes derived from mucochloric or mucobromic acid, and was first observed by Liebermann[3] in studying the oxime of opianic acid. In order to identify the acid with precision, it was extracted from the acidified solution with ether, and the residue obtained by evaporation of the ether was recrystallized from small quantities of water. The white, crystalline acid, when melted at ordinary speed,[4] melted at 127°–129°, and gave the percentage of bromine required for brommaleïc acid.

0.1751 gram substance gave 0.1690 gram AgBr.

[1] This JOURNAL, **16**, 298, 304, 306; Proc. Amer. Acad., **29**, 47, 51, 53.
[2] Proc. Amer. Acad., **29**, 248. [3] Ber. d. chem. Ges., **19**, 2925.
[4] This JOURNAL, **10**, 422; Proc. Amer. Acad., **23**, 219.

	Calculated for $C_4H_3BrO_4$.	Found.
Br	41.03	41.09

The addition of baric hydrate to an aqueous solution of the acid threw down a sandy, granular barium salt, and the supernatant liquid was farther precipitated by the addition of alcohol. By the spontaneous evaporation of its solution, the salt was obtained in spherical aggregations of small prisms. The composition of the salt also agreed tolerably well with the formula given by Wislicenus.[1]

0.2411 gram of air-dried salt gave 0.1517 gram $BaSO_4$.

	Calculated for $BaC_4HBrO_4.2\frac{1}{2}H_2O$.	Found.
Ba	36.54	36.99

Since it was thus shown that brommaleïc acid-aldehyde was formed in considerable quantity from pyromucic acid through the action of three molecules of bromine in aqueous solution, we thought it not impossible that this acid might be isolated directly from the products of the reaction. We found, however, that this product was as unmanageable as that which we had obtained by the action of two molecules of bromine. The viscous liquids could not be brought to crystallization on standing over sulphuric acid, or after extraction with various solvents. An attempt to distil the liquid *in vacuo* brought about complete decomposition. By successive treatment with water and evaporation we succeeded in removing in crystalline form a portion of the mucobromic acid which the viscous liquid contained, but the thick mother-liquors from which no crystals separated on standing, still apparently contained a small amount of mucobromic acid. A determination of bromine in the well dried residue showed too high a percentage of bromine.

0.2961 gram substance dried over H_2SO_4 gave 0.2911 gram AgBr.

	Calculated for $C_4H_3BrO_3$.	Found.
Br	44.69	46.02

We further attempted to obtain a separation by partial neutralization. A solution, partially neutralized with baric car-

[1] Ann. Chem. (Liebig), 246, 57.

bonate, was extracted with ether and the residue left by evaporation of the ether carefully dried as before. A complete analysis of the preparation showed that it contained more than 20 per cent. of mucobromic acid.

I. 0.6359 gram substance dried over H_2SO_4 gave 0.5820 gram CO_2 and 0.1000 gram H_2O.

II. 0.2668 gram substance gave 0.3046 gram AgBr.

	Calculated for $C_4H_3BrO_3$.	Calculated for $C_4H_2Br_2O_3$.	Found. I.	II.
C	26.81	18.60	24.95	....
H	1.64	0.77	1.75	....
Br	44.69	62.02	....	48.60

For the better characterization of the brommaleïc acid-aldoxime, we have prepared several of the salts.

Barium Salt of Brommaleïc Acid-aldoxime, $Ba(C_4H_3BrNO_3)_2.4H_2O$.—This salt was made by the neutralization of the oxime suspended in water by baric hydrate. It is somewhat sparingly soluble in cold water, more readily in hot water, and may be obtained by the spontaneous evaporation of its aqueous solution in long, glassy, friable needles. The air-dried salt contains four molecules of water, three of which it loses over sulphuric acid, while the fourth cannot be driven off by heat without bringing about decomposition.

I. 0.4350 gram air-dried salt lost over H_2SO_4 0.0388 gram H_2O.

II. 0.8269 gram air-dried salt lost over H_2SO_4 0.0742 gram H_2O.

III. 0.3251 gram air-dried salt gave 0.1270 gram $BaSO_4$.

	Calculated for $Ba(C_4H_3BrNO_3)_2.4H_2O$.	I.	Found. II.	III.
$3H_2O$	9.07	8.96	8.97	....
Ba	23.02	....	....	22.97

0.3317 gram salt dried over H_2SO_4 gave 0.1423 gram $BaSO_4$.

	Calculated for $Ba(C_4H_3BrNO_3)_2.H_2O$.	Found.
Ba	25.32	25.22

Lead Salt of Brommaleïc Acid-aldoxime, $Pb(C_4H_3BrNO_3)_2$.—This salt is sparingly soluble in cold water, and may readily be made from a solution of the sodium salt by precipitation;

when crystallized from boiling water it forms fine, sharp, lustrous needles. The air-dried salt lost nothing over sulphuric acid, and gave the percentage of lead required by the anhydrous salt.

0.3558 gram of the salt gave 0.1811 gram $PbSO_4$.

	Calculated for $Pb(C_4H_3BrNO_3)_2$.	Found.
Pb	34.90	34.77

Silver Salt of Brommaleïc Acid-aldoxime, $AgC_4H_3BrNO_3$. — This silver salt is practically insoluble in water, and was made by the addition of argentic nitrate to a solution of the sodium salt. It is precipitated in white, globular aggregations of microscopic crystals, but it soon darkens, even at ordinary temperatures, and is rapidly blackened on heating. Analyses of the salt well washed with cold water, and dried over sulphuric acid, gave a somewhat too low percentage of silver.

I. 0.3039 gram salt gave 0.1868 gram AgBr.

II. 0.2636 gram salt gave 0.1621 gram AgBr.

	Calculated for $AgC_4H_3BrNO_3$.	Found. I.	Found. II.
Ag	35.88	35.31	35.32

Methyl Ester of Brommaleïc Acid-aldoxime, $C_4H_3BrNO_3.CH_3$. —Unlike the oximes of mucobromic and mucochloric acids, brommaleïc acid-aldoxime is not esterified even by long boiling with methyl alcohol. If, however, a very small percentage of concentrated sulphuric acid is added, the ester is formed without difficulty, and is obtained in colorless needles which melt at 152°–153°. On heating the ester dissolves freely in alcohol, less readily in benzol; it is readily soluble in chloroform, sparingly soluble in ether, and almost insoluble in ligroïn; it may be recrystallized without difficulty from hot water.

I. 0.2168 gram substance gave 0.2263 gram CO_2 and 0.0518 gram H_2O.

II. 0.1460 gram substance gave 0.1317 gram AgBr.

	Calculated for $C_4H_3BrNO_3.CH_3$.	Found. I.	Found. II.
C	28.85	28.45	....
H	2.88	2.65	....
Br	38.46	....	38.39

Brommaleïc Acid-aldoxime Anhydride, $C_4H_2BrNO_3$.—When brommaleïc acid-aldoxime is allowed to stand in the cold with concentrated hydrochloric acid, it gradually dissolves, and large irregular crystals of a new body melting at 78°–80° separate. By extracting the mother-liquors with ether, a small additional amount of the same body may be obtained. The yield is small, and is seriously diminished if the action of the acid is too long continued. While we have observed no similar action with concentrated hydrobromic acid, the new body is formed by the action of concentrated sulphuric acid, and it may most readily be made in this way. The oxime dissolves in a small amount of the concentrated acid, and gives a clear, slightly yellow solution. This solution is then poured into a small volume of cold water, care being taken, with good cooling, to prevent any marked elevation of temperature. The crystals which separate are washed with a little cold water, dried, and recrystallized from carbonic disulphide. The yield in this case was somewhat more than 50 per cent. of the theoretical amount. Analysis showed this body to be the anhydride of the oxime.

I. 0.1900 gram substance prepared with H_2SO_4 gave 0.2047 gram AgBr.

II. 0.1256 gram substance prepared with HCl gave 0.1350 gram AgBr.

	Calculated for $C_4H_2BrNO_3$.	Found. I.	II.
Br	45.45	45.84	45.73

The anhydride, when crystallized from carbonic disulphide, melts at 82°–83°. When cautiously heated between watch-glasses it may be sublimed in delicate needles, which melt at 83°; when heated a few degrees above its melting-point, it gives brommaleïnimide. It dissolves very slowly with apparent decomposition in solutions of the alkaline carbonates. This behavior, together with the melting-point, is sufficient to characterize the substance as the anhydride, and distinguish it from the isomeric imide or cyanide.

Mucochloroxime Anhydride, $C_4HCl_2NO_3$.—It seemed to us advisable to try the action of concentrated hydrochloric and sulphuric acids upon mucochloric acid, the anhydride of

which was not obtained by Hill and Cornelison.[1] We followed the methods just described and obtained through the action of each of these acids a body which on analysis proved to be the anhydride.

I. 0.2121 gram substance made with HCl gave 0.3651 gram AgCl.

II. 0.1325 gram substance made with H_2SO_4 gave 0.2289 gram AgCl.

	Calculated for $C_4HCl_2NO_2$.	Found. I.	II.
Cl	42.73	42.55	42.71

Mucochloroxime anhydride crystallizes from carbonic disulphide in irregular aggregations of thick, oblique plates, which melt at 76°–77°. It is readily soluble in alcohol, chloroform or benzol, somewhat sparingly soluble in ether; it dissolves freely in boiling carbonic disulphide, more sparingly in cold; in cold ligroïn it is almost insoluble, but dissolves more freely on heating.

We also made from mucobromoxime, by the action of sulphuric acid, the anhydride melting at 117°–118°, already described.

Brommaleïnimide, $C_4H_2BrNO_2$.—While the oxime of mucobromic and mucochloric acids,[2] like the oximes of the ortho-aldehyde-acids[3] of the aromatic series, yield when heated the corresponding imides by isomerization of the anhydrides first formed, we have been unable to prepare brommaleïnimide by heating directly the brommaleïc acid-aldoxime. It already has been said that the oxime melts with explosive decomposition between 140° and 150°, but from the charred product we found it impossible to isolate the imide. By cautiously heating the anhydride, however, a more satisfactory result is obtained, for the imide may then be separated by repeated sublimation from the carbonaceous residue; still only about one-third of the weight of the anhydride taken was obtained. The product agreed with the description of Ciamician and Silber,[4] and melted at 149°–150°.

[1] This JOURNAL, **16**, 303; Proc. Amer. Acad., **29**, 51.
[2] This JOURNAL, **16**, 299, 304; Proc. Amer. Acad., **29**, 47, 51.
[3] Ber. d. chem. Ges., **19**, 2278, 2293; **24**, 2346; J. Chem. Soc., **57**, 1069.
[4] Ber. d. chem. Ges., **17**, 557; Kiesielinski: Wien. Acad. Ber., 2 Abth., **74**, 565.

In studying the formation of the oxime anhydride, by the action of sulphuric acid, it was noticed that dichlormaleïnimide and dibrommaleïnimide were formed from the corresponding oximes when the acid was allowed to act at 100°, and Liebermann[1] had already observed, in 1886, that hemipinimide could be made in the same way from the oxime of opianic acid. An attempt to prepare brommaleïnimide by the same method gave negative results.

Products Formed from Brommaleïc Acid-aldoxime by Addition.

The conversion of brommaleïc acid-aldoxime into its anhydride, through the action of sulphuric and hydrochloric acids, has already been described. With hydrobromic acid no formation of anhydride was observed, but instead the products then formed were brommaleïc acid with ammonic bromide, or, on long standing, dibromsuccinic acid. The latter acid was more rapidly formed when the solution of the oxime in glacial acetic acid was saturated with gaseous hydrobromic acid. Precisely the same reaction took place when the oxime was dissolved in glacial acetic acid mixed with 20 per cent. of acetic anhydride, and saturated with gaseous hydrochloric acid (Beckmann's mixture). Ammonic chloride was formed and chlorbromsuccinic acid remained in solution. The residue left on evaporation *in vacuo* over lime, was drained on a porous tile, dissolved in ether and precipitated by the addition of chloroform. The acid thus obtained crystallized in clear, rectangularly truncated prisms, which were quite readily soluble in water or alcohol, more sparingly soluble in ether, and difficultly soluble in chloroform or ligroïn. On heating it remained unaltered up to 170°, and then was gradually decomposed without melting.

I. 0.2072 gram substance gave 0.1596 gram CO_2, and 0.0406 gram H_2O.

II. 0.1017 gram substance gave 0.1447 gram AgCl+AgBr.

	Calculated for $C_4H_4BrClO_4$.	Found. I.	II.
C	20.74	21.01	....
H	1.73	2.18	....
Cl + Br	49.87	....	49.57

[1] Ber. d. chem. Ges., 19, 2924.

While we have been unable to prepare addition-products of the oxime itself, either with hydrochloric or with hydrobromic acid, addition-products of the methyl ester can readily be formed from a solution of the oxime in methyl alcohol.

Methyl Ester of Chlorbromsuccinic Acid-aldoxime, $C_4H_4ClBrNO_3.CH_4$.—Brommaleïc acid-aldoxime was dissolved in about five times its weight of methyl alcohol, saturated with gaseous hydrochloric acid. After standing for twenty-four hours the solution was evaporated *in vacuo* over lime, and the residue was washed with ether, dissolved in a little hot alcohol, and filtered from the small amount of ammonic chloride which had been formed through a secondary reaction. The substance left by the alcohol on evaporation was washed with a little cold water, and recrystallized from hot alcohol. Although it is decomposed by long boiling with water, it may also be recrystallized without difficulty from hot water. It crystallized in long, slender, transparent prisms, which melted at 167°–168°. Analysis showed that it had been formed by the addition of hydrochloric acid to the methyl ester of brommaleïc acid-aldoxime.

I. 0.2276 gram substance gave 0.2063 gram CO_2, and 0.0673 gram H_2O.

II. 0.2252 gram substance gave 0.3054 gram AgCl + AgBr and then 0.4339 gram AgI.

III. 0.3597 gram substance gave 18.0 cc. moist nitrogen at 19° and under a pressure of 762 mm.

	Calculated for $C_4H_4ClBrNO_3.CH_3$.	Found. I.	II.	III.
C	24.54	24.71	....	....
H	2.87	3.29	....	....
Br + Cl	47.21	....	47.24	....
Cl	14.50	....	14.80	....
Br	32.71	....	32.25	....
N	5.73	....	....	5.76

Methyl Ester of Dibromsuccinic Acid-aldoxime, $C_4H_4Br_2NO_3.CH_3$.—This substance was formed when a solution of brommaleïc acid-aldoxime in methyl alcohol was saturated with gaseous hydrobromic acid, care being taken to keep the solution cool. On evaporation over lime, a somewhat oily product was obtained, but the liquid portions partially solidified

when it was treated with a little cold water. After drying on a porous plate, the substance may be recrystallized from hot alcohol, or it may also be purified by precipitating with ligroïn, its solution in a mixture of alcohol and ether. From alcohol it crystallizes in narrow, flat prisms, which melt at 161°–162°.

0.1553 gram substance gave 0.2033 gram AgBr.

	Calculated for $C_4H_4Br_2NO_3.CH_3$.	Found.
Br	55.37	55.72

Tribromsuccinic Acid-aldoxime, $C_4H_4Br_3NO_3$.—Preliminary experiments showed that brommaleïc acid-aldoxime could be made to unite directly with bromine, but that this addition could not be effected smoothly at ordinary temperatures, and that great care must be taken to exclude all moisture, in order to obtain satisfactory results. The carefully dried oxime was heated for three or four hours at 75° to 80°, with somewhat more than the theoretical amount of bromine, dehydrated with sulphuric acid and diluted with about twenty times its volume of dry chloroform. Under these conditions, the amount of hydrobromïc acid formed is small, although its formation cannot wholly be avoided, and the product always contains a little dibrommaleïc acid and ammonic bromide. In this way from 80 to 86 per cent. of the theoretical weight of the addition-product may be obtained. The product is a coarsely crystalline cake, insoluble in the chloroform. It may advantageously be washed with cold and afterward with hot benzol; it is best purified by the precipitation of the ethereal solution with ligroïn. It is then obtained in beautiful rectangular plates, which become opaque and friable with loss of weight soon after they are removed from the mother-liquor. The substance melts with decomposition, accompanied by the evolution of bromine and hydrobromic acid, at a temperature which varies greatly with the rate of heating. When heated at ordinary speed it was found to melt at 133°, but when dipped into a bath heated to 150°, fifteen seconds elapsed before melting.

I. 0.2645 gram substance gave 0.1327 gram CO_2, and 0.0280 gram H_2O.

II. 0.1451 gram substance gave 0.2314 gram AgBr.

III. 0.5064 gram substance gave 18.8 cc. moist nitrogen at 23°.2 and under a pressure of 756 mm.

	Calculated for $C_4H_4Br_2NO_2$.	Found. I.	II.	III.
C	13.56	13.69	....	....
H	1.13	1.18	....	....
Br	67.79	....	67.85	....
N	3.96	....	.....	4.16

Dibromacroleïnoxime, $C_3H_3Br_2NO$.—Tribromsuccinic acid-aldoxime, when warmed with water, readily dissolves, but the solution immediately grows turbid with the separation of a more sparingly soluble decomposition-product. If too much water is not used the body separates from the warm solution in fine, felted needles; at the same time carbonic dioxide and hydrobromic acid are formed. For the preparation of this decomposition-product, we have found it advantageous to add the tribromsuccinic acid-aldoxime slowly, with constant stirring, to forty times its weight of water heated to 40°. A part of the product separates at this temperature, and more is obtained as the solution cools. When purified by recrystallization from hot water and dried over sulphuric acid, its percentage composition was found to agree with that of the oxime of dibromacroleïn.

I. 0.3021 gram substance gave 0.1704 gram CO_2 and 0.0372 gram H_2O.

II. 0.1597 gram substance gave 0.2630 gram AgBr.

III. 0.2953 gram substance gave 16.4 cc. moist nitrogen at 20°.2 and under a pressure of 759 mm.

	Calculated for $C_3H_3Br_2NO$.	Found. I.	II.	III.
C	15.72	15.38	....	....
H	1.31	1.37	....	....
Br	69.87	....	70.08	....
N	6.11	....	....	6.34

Dibromacroleïnoxime is readily soluble in alcohol, ether, chloroform, benzol, or carbonic disulphide, but sparingly soluble in ligroïn. It dissolves freely in hot water and almost wholly separates as the solution cools, in slender, tufted needles. When purified by recrystallization from

boiling ligroïn, in which, however, it is but sparingly soluble, it melted quite sharply at 104°; but material recrystallized from water, gave a somewhat lower melting-point. It dissolves readily in solutions of the alkaline hydrates, but not in solutions of the alkaline carbonates.

Tribromsuccinic acid-aldoxime is evidently decomposed on heating with water according to the equation,

$$C_4H_4Br_3NO_3 = C_3H_3Br_3NO + CO_2 + HBr.$$

This mode of decomposition is identical with that observed by Petrieff[1] in the case of the analogous tribromsuccinic acid.

$$C_4H_3Br_3O_4 = C_3H_3Br_3O_2 + CO_2 + HBr.$$

The yield of crude product, which may be thus obtained from tribromsuccinic acid-aldoxime, amounts to 90 per cent. of the weight calculated according to the above equation.

Dibromacroleïn.—Although the dibromacroleïnoxime may be recrystallized from hot water without difficulty, it is decomposed by prolonged boiling of the solution; the same decomposition is more readily effected by heating with dilute hydrochloric acid; in either case a sharp acroleïn-like odor is developed. In order to identify the products formed, the oxime was heated with dilute hydrochloric acid and the solution distilled with steam until the liquid in the retort was free from odor. This solution was then evaporated to dryness on the water-bath, and the residue washed with ether. Alcohol then dissolved hydroxylamine hydrochlorate, which reduced Fehling's solution in the cold and precipitated brommaleïc acid-aldoxime from a solution of the acid. Whenever crude tribromsuccinic acid-aldoxime was thus boiled with dilute hydrochloric acid, and distilled with steam, dibrommaleïc acid was found in the ethereal washings of the retort-residue, and was identified through the melting-point (114°-115°) of its anhydride, and the character of its barium salt. The aqueous distillate gave the familiar reactions for aldehydes, and with hydroxylamine hydrochlorate it again yielded the dibromacroleïnoxime, melting at 104°. From this solution,

[1] Ann. Chem. (Liebig), **193**, 70.

however, we were unable to isolate the aldehyde in analyzable form. It could readily be extracted with ether, but, on drying over sulphuric acid, the colorless oil was converted into a viscous, tarry product, which did not invite to farther study. We therefore determined to convert the aldehyde directly into the corresponding dibromacrylic acid, which we thought would present no difficulties in purification and identification. The dilute aqueous solution obtained by distillation with steam was, therefore, warmed with an excess of well-washed argentic oxide. Metallic silver was formed in abundance, together with a soluble silver salt. The residue was thoroughly extracted with hot water, the dissolved silver precipitated with hydrochloric acid, and the filtered solution then extracted with ether. The crude product obtained by the evaporation of the ether closely resembled α-β-dibromacrylic acid, but the yield was very small—not more than 10 to 15 per cent. of the theoretical quantity—the melting-point was low, and the analytical results unsatisfactory. Like α-β-dibromacrylic acid, this acid formed a sparingly soluble acid potassium salt, which crystallized in long, silky needles; the acid, separated from this acid potassium salt, crystallized from ligroïn in stout prisms, which melted at 83°–84°, but we were unable to raise this melting-point by further treatment to the proper point, 85°–86°. The silver salt of the acid formed fine, felted needles, which could be recrystallized unchanged from hot water. A direct comparison of this acid with the α-β-dibromacrylic acid from mucobromic acid,[1] and with the dibromacrylic acid of Fittig and Petri,[2] left no doubt in our minds that we had in our hands the former acid. The small yield and the unexpected difficulties which we met in its purification, made us unwilling to sacrifice the time and material necessary for its more rigorous identification. Evidently the chief importance of further study lay in the fact that tribromsuccinic acid-aldoxime had apparently given a dibromacrylic acid which was isomeric with the acid which may be obtained by a similar reaction from tribromsuccinic acid.

[1] This JOURNAL, **3**, 113; **4**, 169: Proc. Amer. Acad., **16**, 192; **17**, 125.
[2] Ann. Chem. (Liebig), **195**, 70.

Chlormaleïc Acid-aldoxime.

The isolation of a crystalline chlormaleïc acid-aldehyde presents the same difficulties which we met in attempting to prepare the corresponding body containing bromine; the oxime derived from it, however, may easily be made. In order to bring the proper amount of chlorine into reaction, we used the method already described by one of us for the preparation of mucochloric acid.[1] Pyromucic acid was suspended in twenty times its weight of concentrated hydrochloric acid, and the calculated amount (three molecules) of finely powdered manganic dioxide of known strength was slowly added, with careful cooling. After standing for several days, the solution was filtered, diluted, and extracted with ether. On evaporation the ether left a viscous uncrystallizable residue, which was treated with small quantities of cold water, and from this aqueous solution the oxime could easily be obtained by the action of hydroxylamine hydrochlorate. It could hardly be distinguished from the brommaleïc acid-aldoxime, which we have already described. Its behavior toward solvents was also the same, except that it was still more sparingly soluble in ligroïn, and could, therefore, more readily be purified by precipitation with ligroïn from its ethereal solution. When heated in the ordinary way it melted at 150° with decomposition.

I. 0.3165 gram substance gave 0.3711 gram CO_2 and 0.0897 gram H_2O.[2]

II. 0.2009 gram substance gave 0.1943 gram AgCl.

III. 0.3139 gram substance gave 27.2 cc. moist nitrogen at 28° and under a pressure of 760 mm.

	Calculated for $C_4H_4ClNO_2$.	Found. I.	II.	III.
C	32.18	31.98	....	....
H	2.68	3.15	....	....
Cl	23.72	....	23.92	....
N	9.36	....	....	9.51

In order to establish the relation of the oxime to chlormaleïc acid, it was heated with water in a sealed tube for sev-

[1] This JOURNAL, 9, 160; Proc. Amer. Acad., 22, 327.

[2] In order to avoid explosive combustion, the substance must be mixed with a large amount of powdered copper oxide.

eral hours at 110°. The somewhat colored aqueous solution was concentrated, acidified with hydrochloric acid, and extracted with ether. As the acid left by the ether was quite dark colored, it was neutralized with baric hydrate, the barium salt precipitated by alcohol, and the acid again liberated from this purified salt. The colorless acid thus obtained gave the percentage of chlorine required by chlormaleïc acid.

0.1667 gram substance gave 0.1572 gram AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.57	23.32

The melting-point of the acid also agreed with the observations of Zincke[1] and van der Riet.[2] In one case the carefully dried acid melted at 106°; another preparation repeatedly recrystallized from water, and dried over sulphuric acid, did not soften below 100°, and melted quite sharply at 111°. Zincke's acid softened at 95° and melted at 106°. Probably the melting-point of chlormaleïc acid, like that of brommaleïc acid, varies with the rate with which it is heated. For the further identification of the acid the barium salt was analyzed.

0.4157 gram of the air-dried salt gave 0.2982 gram $BaSO_4$.

	Calculated for $BaC_4HClO_4.2H_2O$.	Found.
Ba	42.62	42.18

Chlormaleïc Acid-aldoxime Anhydride, $C_4H_4ClNO_3$.—Like the corresponding compound containing bromine, the oxime anhydride can readily be made by the action of concentrated sulphuric acid at ordinary temperatures. The oxime was dissolved in about twice its weight of acid, and the solution slowly poured, with constant shaking and cooling, into cold water. The anhydride at once separates, but as it is somewhat soluble in the diluted acid, the solution may profitably be extracted with ether. The anhydride is readily soluble in the ordinary solvents, except ligroïn. It may conveniently be recrystallized from carbonic disulphide, and forms then brilliant transparent scales which melt at 58°.

0.1814 gram substance gave 0.1978 gram AgCl.

[1] Ber. d. chem. Ges., **26**, 508.
[2] Ann. Chem. (Liebig), **280**, 227.

	Calculated for $C_4H_3ClNO_3$.	Found.
Cl	26.98	26.97

Methyl Ester of Chlormaleïc Acid-aldoxime, $C_4H_3ClNO_3.CH_3$.—The oxime was dissolved in methyl alcohol, a small percentage of concentrated sulphuric acid added, and the solution boiled with reverse condenser for several hours. The ester crystallized in finely felted needles, which may be recrystallized from hot water or alcohol, and which melt at 130°.

0.1713 gram substance gave 0.1502 gram AgCl.

	Calculated for $C_4H_3ClNO_3.CH_3$.	Found.
Cl	21.69	21.68

Methyl Ester of Dichlorsuccinic Acid-aldoxime, $C_4H_4Cl_2NO_3$. CH_3.—This substance was made by saturating with gaseous hydrochloric acid a carefully cooled solution of the oxime in methyl alcohol. After standing for several days the solution was evaporated *in vacuo* over lime. The semi-solid residue contained ammonic chloride as the product of a secondary reaction; on the addition of water an oil separated which solidified on cooling, but melted again at ordinary temperatures. The oil was, therefore, taken up with ether, the ethereal solution dried with calcic chloride, and again evaporated *in vacuo*; the residue was then freed from oily products by draining on a porous plate. When recrystallized from alcohol, in which it is quite readily soluble, the substance melted at 135°.

0.1058 gram substance gave 0.1511 gram AgCl.

	Calculated for $C_4H_4Cl_2NO_3.CH_3$.	Found.
Cl	35.46	35.31

By the action of gaseous hydrobromic acid upon a solution of the oxime in methyl alcohol can be formed a body which melts at 145°, and which is doubtless the methyl ester of a bromchlorsuccinic acid-aldoxime, isomeric with the body already described, as formed under similar conditions from brommaleïc acid-aldoxime by the action of hydrochloric acid. It has not been further examined.

CII.—ON THE ABSORPTION OF OXYGEN BY TETRABROMFURFURAN.

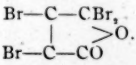
By Henry A. Torrey.

In 1885 Hill and Hartshorn[1] found the α-dibromfurfuran, which they then described, was readily oxidized upon exposure to the air, and they showed that maleïc acid was formed, together with hydrobromic acid, when the oxidation took place in the presence of water. Although tetrabromfurfuran also contains two bromine atoms in the α-position, it may be exposed to the air indefinitely, under ordinary conditions, without essential alteration. The accidental discovery that exposure to direct sunlight quickly brought about a marked change in the physical properties of this body suggested the probability that in this case also the alteration in properties was due to oxidation. At the request of Professor H. B. Hill I made this behavior of tetrabromfurfuran the subject of further study.

Preliminary experiments soon showed that the changes in properties were accompanied by an increase in weight, and that the reaction ran much more rapidly with undiluted oxygen. While the oxidation was more quickly ended at high temperature, the reaction appeared to be more neatly effected at ordinary temperature. The best results were obtained with dry air or oxygen, since the presence of moisture or the vapor of alcohol checked or hindered the reaction. The time required to complete the reaction could materially be diminished by the use of a concave mirror to concentrate the sunlight. Under the most favorable conditions a gain in weight was noted in six or seven hours, which amounted to 80 or 85 per cent. of that required by the addition of one atom of oxygen to each molecule of the tetrabromfurfuran. An examination of the products formed, however, showed that the oxidation was nearly complete, and that the deficit in weight was due to the partial conversion of the dibrommaleyl bromide, which was first formed in the reaction, into dibrommaleïc anhydride. That this conversion was not due to insufficient drying of the oxygen was shown by the fact that sensible

[1] Ber. d. chem. Ges., 18, 448.

quantities of bromine were liberated, if the oxidation was too long continued, and that the presence of free bromine could then be established by the ordinary qualitative tests. The main product of the reaction proved to be the dibrommaleyl bromide, melting at 58°–59°, which was described by Hill and Cornelison.[1] As this body was made by them through the action of bromine upon dibromcrotonolactone, into which it could again be converted by reduction, its structure may be taken to be



Since the bromine of the dibrommaleyl bromide is directly replaceable by oxygen, its formation from the symmetrical tetrabromfurfuran is also probably due to the displacement of bromine at the outset; the bromine, however, is at first immediately taken up and is thus transferred from one α-carbon to the other without breaking the furfuran ring.

The tetrabromfurfuran used in the course of this work was made by the action of an alcoholic solution of potassic hydrate upon the dibromfurfurantetrabromide described by Hill and Sanger[2] and afterwards further studied by Hill and Hartshorn.[3] It was colorless, well crystallized, and had the proper melting-point, 64°–65°. Since preliminary experiments had shown that complete oxidation could be effected in a much shorter time by the use of undiluted oxygen, no extended experiments were made with air. A weighed quantity of tetrabromfurfuran was introduced into a small, tared flask, which was then connected through sulphuric acid drying-tubes with a gas-holder containing oxygen; a second sulphuric-acid tube passed through the cork of the flask established communication with the atmosphere. After the air contained in the flask had been displaced by dry oxygen, the flask was set in direct sunlight, and the gas-holder so adjusted that the oxygen within the flask was approximately at atmospheric pressure. The tetrabromfurfuran soon turned bright

[1] This JOURNAL, **16**, 207; Proc. Amer. Acad., **20**, 21.
[2] Proc. Amer. Acad., **21**, 145; Ann. Chem. (Liebig), **232**, 55.
[3] Ber. d. chem. Ges., **18**, 449.

yellow, gradually lost its crystalline structure, and finally became viscous. From time to time the oxygen was driven out by dry air, and the change in weight determined. After six or seven hours of exposure, the maximum, corresponding to from 80 to 85 per cent. of one atom of oxygen, was usually reached, and soon after a loss of weight was observed. The flask was then seen to be filled with the vapor of bromine, which when displaced by dry air, liberated iodine from potassic iodide. Aside from the preliminary tests, five experiments were made with 26.7 grams of tetrabromfurfuran in all. In the first two cases the flask with its contents was heated to 100°; in the remaining three the flask was set upon a white porcelain tile, and the illumination increased by a concave mirror, but no attempt was made to control the temperature. In two out of the three last experiments the liberation of bromine was noticed. In all cases the final product was a reddish-yellow, semi-liquid mass, which solidified completely on standing. On boiling with water the greater part gradually dissolved, and, on distillation with steam, a small amount of unaltered tetrabromfurfuran was usually found in the distillate. The aqueous solution left in the retort contained, beside hydrobromic acid, dibrommaleïc acid. The liquid was neutralized with baric carbonate, the baric dibrommaleate precipitated by alcohol, dried, and finally recrystallized from water. The air-dried salt then contained the proper percentage of barium.

I. 0.4246 gram air-dried salt gave 0.2193 gram $BaSO_4$.

II. 0.1902 gram air-dried salt gave 0.0992 gram $BaSO_4$.

	Calculated for $BaC_4Br_2O_4.2H_2O$.	Found. I.	II.
Ba	30.78	30.36	30.66

The free acid was extracted from its aqueous solution by ether, and converted into its anhydride by sublimation. The melting-point of the anhydride was then found to be 113°–114°, while dibrommaleïc anhydride melts at 115°.

Although there could be little doubt that the original oxidation-product contained dibrommaleyl bromide, it seemed advisable to make some attempt to isolate it. On distillation

under diminished pressure, the crude product gave a colorless distillate, which passed over at about 140° under a pressure of 25 mm. On cooling in a freezing-mixture, this distillate partially solidified, and by filtration a crystalline substance was obtained, which after recrystallization from ligroïn, melted at 115°. This melting-point and the behavior toward water was sufficient proof that the body was dibrommaleïc anhydride. The liquid filtrate was then mixed with ligroïn, with the hope of separating more of the anhydride, but as it remained clear, the ligroïn was allowed to evaporate spontaneously. On long standing, a few tabular crystals appeared, which, after careful pressing, melted at 58°–59°. Since Hill and Cornelison had found that dibrommaleyl bromide is very slowly attacked by cold water, while dibrommaleïc anhydride is soon converted into the acid, a fresh portion of the crude oxidation-product was finely powdered, and shaken with successive portions of cold water. The aqueous solution contained dibrommaleïc acid, while the insoluble residue could then be recrystallized from ligroïn. Even after repeated recrystallization, the melting-point of the crystalline product could not be raised above 51°–52°, and analysis showed too high a percentage of bromine. On decomposing the body with hot water and distilling with steam, the presence of tetrabromfurfuran could be established, but no means could be found to remove it without decomposing the dibrommaleyl bromide. The presence of the latter body was satisfactorily proved, however, by the formation of dibromcrotonolactone, melting at the proper point (90°–91°), when the substance was reduced with stannous chloride and hydrochloric acid.

Contributions from the Sheffield Laboratory of Yale University.

LIII.—ON HALOGEN ADDITION-PRODUCTS OF THE ANILIDES.

[THIRD PAPER.]

By H. L. Wheeler, Bayard Barnes and J. H. Pratt.

In a recent paper from this laboratory[1] it was shown that the anilides are capable of forming addition-products with bromine and iodine, and that these addition-products can only be formed in the presence of a halogen acid. They are, therefore, perhalides, and it was concluded that these compounds are derivatives of substituted ammonium salts, and that they are perfectly analogous to the perhalides of caesium[2] and ammonium.[3]

We have continued the study of these compounds in order to test the correctness of this view, and also with the object of determining the structure of the halogen salts of the anilides. We have made crystallographic measurements of some of the perhalides and of ammonium triiodide, and we find that, although ammonium triiodide is perfectly analogous to the perhalides of the alkali metals, on the other hand, the perhalides of the anilides, as far as examined, show no crystallographic analogy whatever with these compounds.

This, perhaps somewhat unexpected, result would indicate that the peculiar salts from which the perhalides are derived, are not substituted ammonium compounds, and it will be seen below that other experimental work confirms this conclusion.

All these perhalides are derivatives of two molecules of an anilide with one of a halogen acid, or, briefly, of the 2 : 1 salts. Perhalides derived from 1 : 1 salts have not been prepared. When these salts are employed, the products obtained are invariably derivatives of 2 : 1 salts. However, no special attempt has been made to decide whether the 1 : 1 salts are capable of forming perhalides.

Nölting and Weingärtner[4] were the first to prepare a 2 : 1 salt of the anilides. They found that acetanilide and hydro-

[1] Wheeler and Walden: This Journal, 18, 85.
[2] Wells: Am. J. Sci., 43, 17.
[3] Roozeboom: Ber. d. chem. Ges., 14, 2398.
[4] Ber. d. chem. Ges., 18, 1340.

gen chloride gave a compound represented by the formula $(C_6H_5NHCOCH_3)_2HCl$, and they investigated its behavior on heating. At 250° they obtained ethenyldiphenylamidine, at 280° flavaniline, and at 300° dimethylquinoline. The 1 : 1 hydrochloride of acetanilide was observed by Knorr.[1]

Our work with these salts has shown that the anilides in general form these two series of salts, and no other types have been observed. The anilides differ from their pseudo derivatives, *i. e.*, the imidoesters, both in forming 2 : 1 salts, as well as in not forming 1 : 2 salts. These salts are characteristic for the two series. It is now interesting to note that formanilide gives 2 : 1 salts in the same manner in which the corresponding salts of the other anilides are obtained. The conclusion that follows from this is that formanilide belongs to the series of anilides, and that it has the normal structure.

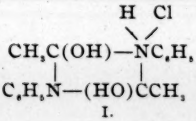
At present there is no occasion to assume that the 1 : 1 salts are anything but substituted ammonium compounds. In the case of the 2 : 1 salts, it is different, and here numerous constitutional formulas are theoretically possible. It will be convenient to discuss these under three heads:

I.—Those which are represented as having the pseudo form of the anilide.

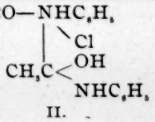
II.—Those in which oxygen or the acyl group takes part in the union of the molecules.

III.—The diammonium structure.

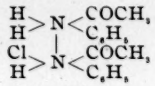
The following formulas are examples of these types:



I.



II.



III.

The first type is excluded, since we find that methylmeta-

[1] Ann. Chem. (Liebig). **245**, 375.

nitroacetanilide gives perhalides of a 2 : 1 salt, and also since this is an ammonium salt.

In regard to the second type, it may be stated that the presence of oxygen, *i. e.*, an acyl group, is unnecessary for the formation of 2 : 1 salts, or of their perhalides. Troost[1] has prepared the compounds $2NH_4.HBr$ and $2NH_4.HI$, and Grimaux[2] has described a perhalide of pyridine represented by the following formula: $(C_5H_5N)_2HBr.Br_4$. Another compound that evidently belongs to this class is the iodine addition-product of benzamide obtained by Curtius:[3]

$$C_6H_5CONH_2.I$$
$$|$$
$$C_6H_5CONH_2.I$$

On account of these facts, and since the 2 : 1 salts of the anilides are not derived from the pseudo form, the diammonium structure III seems to be most satisfactory. This structure readily allows for the formation of 2 : 1 salts from the secondary anilides, and also explains the lack of analogy of the perhalides to those of ammonium.

A comparison of the perhalides of the anilides with those of the alkali metals, shows other interesting differences besides the lack of analogy in crystalline form.

In this paper we describe mixed perhalides, and show that the hydrochloric acid salts of the anilides readily give perhalides with iodine, while the corresponding perhalides of the alkali metals could not be obtained.

In the case of the bromides and iodine only $CsBrI_4$[4] could be obtained, rubidium and potassium having little or no tendency to form this perhalide. On the other hand, the hydrobromides of the anilides readily unite with iodine. Methylmetanitroacetanilide hydrobromide giving a tetra addition-product.

The relative stability of these perhalides is similar to those of the alkali metals, those containing only iodine being the most stable. Large crystals of the compound $(C_6H_5NHCOCH_3)_2HI.I_2$, after standing in a corked tube for over a year, gave excellent reflections on the goniometer.

[1] Compt. rend., **92**, 715.
[2] Bull. Soc. Chim. (Paris), **38**, 127.
[3] Ber. d. chem. Ges., **23**, 3040.
[4] Wells: *Loc. cit.*

The property of forming perhalides, and the relatively greater stability of these perhalides, when compared to some of the alkaline metal derivatives, show that it is not basicity that determines their stability or tendency to form, since the salts of the anilides are decomposed by water.

Experimental Part.

Ammonium Triiodide, $NH_4I.I_2$.—This salt was prepared by dissolving the calculated amount of iodine in a strong solution of ammonium iodide and evaporating by standing over potash, as described by Johnson,[1] when dark blue prisms were obtained. These belong to the orthorhombic system and the faces which were observed are as follows:

a, 100.	*c*, 001.	*d*, 011.	*i*, 103.
b, 010.	*m*, 110.	*e*, 102.	

The axial ratio derived from the angles marked with an asterisk in the table below is:

$$a : b : c = 0.6950 : 1 : 1.1415.$$

The crystals are somewhat peculiar in their development, for they show two very similar forms which have no faces alike. They attained a length of 3 mm.

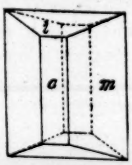


Fig. 1.

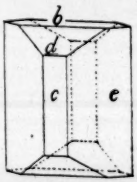


Fig. 2.

Fig. I represents the first form, where the prism *m*, 110 and the dome *i*, 103, are about equally developed, giving the crystals nearly a square outline. The second form of crystals, Fig. II, has nearly the same outline, due to the nearly equal development of the domes *d*, 011 and *e*, 102. The base *c*, 001 has been drawn in front in order to show, to better advantage, the similarity between the two forms. The crystals were

[1] Ber. d. chem. Ges., II, 1268.

generally well developed, but the faces were apt to be dull and somewhat rounded, so that in some cases only approximate measurements could be obtained.

The similarity in the crystallization of ammonium triiodide and the alkali metal trihalides, described by Wells, Wheeler and Penfield[1] is very striking, and in the following table the corresponding angles of the alkali triiodides are given for comparison:

	Measured.	NH_4I_3.	Calculated.	KI_3.	RbI_3.	CsI_3.
$110 \wedge \bar{1}10$, $m \wedge m'''$	*69° 36′			70° 34′	68° 53′	68° 37′
$102 \wedge \bar{1}02$, $e \wedge e'$	*78° 50′				78° 38′	78°
$100 \wedge 011$, $c \wedge d$	48° 26′–48° 45′		48° 47′		48° 19′	47° 51′
$102 \wedge 011$, $e \wedge d$	60° 3′		59° 24′			
$103 \wedge \bar{1}03$, $i \wedge i'$	57° 15′		57° 30′			
c', axis,		1.1415			1.1234	1.1051
a, axis,		0.6950	0.7065		0.6858	0.6824

From the above the ammonium triiodide is shown to be isomorphous with the alkali metal trihalides, while the trihalides of the anilides, as far as examined, show no similarity whatever with the above, the latter crystallizing in either the monoclinic or the triclinic system.

Experiments with Acetanilide.

The 2 : 1 and 1 : 1 *hydrochlorides* of acetanilide[2] separate from an ethyl-acetate or a chloroform solution as a granular precipitate, generally in the form of a mixture, when the solutions are treated with dry hydrogen chloride. The simple salt of the anilides were not obtained in crystals suitable for measurement.

The *Iodhydrochloride*, $(C_6H_5NHCOCH_3)HCl.I_2$.—This salt, as well as the other perhalides described in this paper, was prepared by dissolving the constituents (either the 2 : 1 or 1 : 1 salts and the halogen) in hot glacial acetic acid, and then cooling. The crystals for measurement were generally obtained by slowly evaporating the solution in glacial acetic acid over potassium hydroxide in a desiccator. Better crystals were obtained in this manner than by slowly cooling in a felt box. The crystals in each case were washed free from

[1] Am. J. Sci. [III], **43**, 17 and 478. [2] *Loc. cit.*

acetic acid by means of chloroform, and after drying by pressing on paper, were analyzed. The analytical results have been obtained in the gravimetric way ; determination of mixed halogens have been made by igniting the silver salts in a current of chlorine in the usual manner.

Acetanilide iodhydrochloride, prepared as above, separated in the form of dark-blue, shining needles ; crystals suitable for measurement were not obtained. This and the corresponding salt of parabromacetanilide are the least stable of the perhalides ; they soon lose iodine and turn white.

	Calculated for $C_{16}H_{18}N_2O_2.HCl.I_2$.	Found.
I	45.3	45.9
Cl	6.3	6.6

The 1 : 1 *Hydrobromide*, $C_6H_5NHCOCH_3.HBr$.—This was obtained as a colorless crystalline precipitate. It apparently contained a slight admixture of the 2 : 1 salt.

	Calculated for $C_8H_9NO.HBr$.	Found.
Br	37.0	35.1

The *iodhydrobromide*, $(C_6H_5NHCOCH_3)_2HBr.I_2$, prepared from the above salt, separated in dark-red prisms.

	Calculated for $C_{16}H_{18}N_2O_2.HBr.I_2$.	Found.
I	41.9	41.2
Br	13.2	13.4

The crystallization of acetanilide iodhydrobromide is triclinic, and the following faces have been observed :

c, 001.	*m*, 110.	*p*, $1\bar{1}1$.
b, 010.	*M*, $1\bar{1}0$.	*x*, 403.

The axial ratio derived from the angles marked by the asterisk in the table below was found to be :

$$a : b : c = 0.5707 . 1 : 1.2005 ; \ \alpha = 89° 26',$$
$$\beta = 132° 20', \ \gamma = 83° 16'.$$

The crystals were small, not over 1.5 mm. in length, and were generally doubly terminated. Fig. 3 represents the form of the crystals.

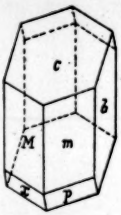


Fig. 3.

The faces were smooth, and gave fair reflections of the signal on the reflecting goniometer. In the table of angles the two extremes of three or more measurements are given.

		Measured.	Calculated.
$c \wedge m$	$001 \wedge 110$	*52° 6′	
$c \wedge b$	$001 \wedge 0\bar{1}0$	*83° 2′	
$c \wedge p$	$001 \wedge \bar{1}11$	*66° 3′	
$c \wedge M$	$001 \wedge 1\bar{1}0$	50° 36′–50° 58′	50° 47′
$m \wedge b$	$\bar{1}10 \wedge 0\bar{1}0$	74° 50′–74° 55′	74° 55′
$m' \wedge p$	$\bar{1}10 \wedge \bar{1}11$	61° 48′–61° 49′	61° 51′
$b \wedge m$	$0\bar{1}0 \wedge 1\bar{1}0$	*58° 11′	
$m \wedge M$	$110 \wedge 1\bar{1}0$	*46° 54′	

The 2 : 1 *Hydroiodide*, $(C_6H_5NHCOCH_3)_2HI$.—This, and not the 1 : 1 salt, was obtained, both from chloroform and ethyl-acetate solutions of the anilide, on saturating with hydrogen iodide. It is a noticeable fact that hydrogen iodide forms 2 : 1 salts more readily than the other halogen acids.

The *Iodhydroiodide*, $(C_6H_5NHCOCH_3)_2HI.I_2$.—This and the above hydroiodide were described in a previous paper. This perhalide has the greatest tendency to crystallize, some of the crystals being 3 mm. in diameter and 10 mm. in length. They crystallize in the triclinic system, and only three faces were observed which could be determined. These have been taken as the three pinacoids, *c*, 001 ; *b*, 010 ; and *a*, 100. On a few crystals other faces were observed, but they could not be identified.

The inclinations of the axes calculated from the angles of pinacoids, are as follows:

$$\alpha = 102° 56′ ; \ \beta = 104° 34′ ; \ \gamma = 113° 2′.$$

$a \wedge b$	$100 \wedge 010$	61° 40′
$a \wedge c$	$100 \wedge 001$	67° 47′
$b \wedge c$	$010 \wedge 001$	68° 47′

Experiments with Parabromacetanilide.

The 2 : 1 *Hydrochloride*, $(C_6H_4.Br.NHCOCH_3)_2HCl$.—The formation of 1 : 1 salts in the case of parabromacetanilide was not observed. This compound was obtained as a colorless, crystalline precipitate.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HCl$.	Found.
Cl	7.6	6.6

The *Iodhydrochloride*, $(C_6H_4Br.NHCOCH_3)_2.HCl.I_2$ was obtained as dark-violet needles.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HCl.I_2$.	Found.
I	35.3	35.3
Cl	4.9	5.2

The 2 : 1 *Hydrobromide*, $(C_6H_4BrNHCOCH_3)_2HBr$, previously described, gave:

The *Iodhydrobromide*, $(C_6H_4BrNHCOCH_3)_2HBr.I_2$, in the form of red prisms.

	Calculated for $C_{16}H_{16}N_2O_2Br_2HBr.I_2$.	Found.
I	33.2	31.1
Br	10.5	10.6

The 2 : 1 *Hydroiodide*, $(C_6H_4BrNHCOCH_3)_2HI$, was obtained as a colorless, crystalline precipitate.

	Calculated for $C_{16}H_{16}N_2O_2Br_2.HI$.	Found.
I	22.8	22.3

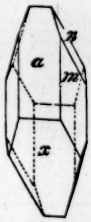


Fig. 4.

The *Iodhydroiodide*, $(C_6H_4BrNHCOCH_3)_2HI.I_4$, prepared from the above, separated in dark-red, triclinic crystals. These attained a diameter of 0.5 mm. The faces observed are the following :

a, 100 ; *m*, 110 ; *x*, $\bar{1}01$; *n*, 011.

The faces were smooth and bright and gave good reflections. From the angles marked by an asterisk in the table below, the following axial ratio was determined :

$$a : b : c = 1.853 : 1 : 3.015 ; \quad \beta = 79° \tfrac{1}{2}'.$$

		Measured.	Calculated.
$a'\wedge n$	$\bar{1}00\wedge 0\bar{1}1$	*93° 30′	
$m\wedge n'$	$1\bar{1}0\wedge\bar{0}11$	*142° 40′	
$a\wedge m$	$\bar{1}00\wedge 1\bar{1}0$	*61° 31′	
$a'\wedge x$	$\bar{1}00\wedge\bar{1}01$	34° 28′	34° 24′
$m'''\wedge d'$	$\bar{1}10\wedge\bar{0}11$	30° 28′	30° 43′
$d\wedge x$	$011\wedge\bar{1}01$	82° 47′	82° 45½′
$m'\wedge x$	$\bar{1}\bar{1}0\wedge\bar{1}01$	66° 35′	66° 35½′
$m''\wedge d'$	$\bar{1}10\wedge 0\bar{1}1$	36° 44′	36° 46′

The *Iodhydroiodide*, $(C_6H_4BrNHCOCH_3)_2HI.I_4$, was obtained in the form of deep-red, monoclinic twins. Enough faces were not shown to permit of satisfactory crystallographic description.

	Calculated for $C_{16}H_{14}N_2O_2Br_2HI.I_4$.	Found.
I	59.68	59.75

Experiments with Methylmetanitroacetanilide.

The 1 : 1 *Hydrobromide*, $C_6H_4NO_2NCH_3COCH_3.HBr$.—This and not the 2 : 1 salt was obtained directly in the form of a colorless, crystalline precipitate.

	Calculated for $C_9H_{10}N_2O_3.HBr$.	Found.
Br	29.0	28.3

The *Bromhydrobromide*, $(C_6H_4NO_2NCH_3COCH_3)_2HBr.Br_2$. —The above 1 : 1 salt gave this perhalide in the form of small dark-yellow, well-developed, stout prisms. It slowly evolves bromine on exposure.

	Calculated for $C_{18}H_{20}N_4O_6HBr.Br_2$.	Found. I.	Found. II.
Br	38.1	37.2	37.4

The *Iodhydrobromide*, $(C_6H_4NO_2NCH_3COCH_3)_2HBr.I_4$.—This was obtained as a black mass, which under the microscope appeared to consist of needles. The powder was dark bottle-green.

	Calculated for $C_{28}H_{30}N_4O_4HBr.I_4$.	Found.
Br	8.1	8.1
I	51.9	52.8

When hydrogen iodide was passed into an ethyl acetate solution of methylmetanitroacetanilide, the acid was reduced and no precipitate was formed.

Experiments with Formanilide.

The 2 : 1 *Hydrochloride*, $(C_6H_5NHCHO)_2HCl$.—When hydrochloric acid is passed into a solution of formanilide in dry benzene, the product obtained is generally a mixture of the 2 : 1 and 1 : 1 salts. The 2 : 1 salt was obtained as a colorless, crystalline precipitate, which soon absorbed moisture and decomposed on exposure.

	Calculated for $C_{14}H_{14}N_2O_2.HCl$.	Found.
Cl	12.7	12.3

The 2 : 1 *Hydroiodide*, $(C_6H_5NHCHO)_2HI$.—The salt, obtained apparently in the form of needles from a benzene solution, rapidly absorbs moisture from the air, becoming sticky and decomposing. For analysis it was rapidly pressed on paper and dried over sulphuric acid in a vacuum-desiccator. The analysis indicates that a slight decomposition was not avoided :

	Calculated for $C_{14}H_{14}N_2O_2HI$.	Found.
I	34.3	31.2

The 1 : 1 *Hydroiodide*, $C_6H_5NHCHO.HI$, differs decidedly in appearance from the above 2 : 1 salt. It separates from an ethyl-acetate solution in granular condition, and is more stable. An iodine determination gave 48.0 per cent. of the halogen instead of the 51.0 per cent.

Attempts were made to prepare perhalides from the salts of formanilide, but when these were warmed in glacial acetic acid the anilide was saponified. Similar results were obtained with the salts of paraformtoluide, the salts of the formyl com-

pounds being considerably less stable than those containing the acetyl group.

Other Experiments.

The 2 : 1 *Hydrochloride*, $(C_6H_4NO_2NHCOCH_3)_2HCl$, was obtained from a chloroform-solution of metanitroacetanilide and hydrogen chloride.

	Calculated for $C_{16}H_{14}N_4O_6.HCl$.	Found.
Cl	8.9	8.7

Under similar conditions methylacetanilide, diphenylbenzamide, diethylbenzamide, and methylbenzanilide gave no precipitate with either hydrogen chloride or bromide, ethyl acetate or chloroform being used as the solvent. Benzamide was not precipitated from a chloroform solution by hydrogen chloride, although this amide gives salts with the halogen acids. From ethyl acetate hydrogen chloride and bromide precipitated the 1 : 1 salts of paraformtoluide, and from benzene, benzamide was precipitated as a 1 : 1 salt by hydrogen iodide.

NEW HAVEN, May, 1897.

ON THE PERMEATION OF HOT PLATINUM BY GASES.

BY WYATT W. RANDALL.

In connection with a research which has been in progress for some time, and in which the attempt is being made to prepare absolutely pure hydrogen for spectroscopic examination, the author has endeavored to free the gas from impurities by filtering it through a diaphragm of hot platinum. The spectroscopic results obtained will be published later; it seemed worth while, however, to give at this time a short account of the work which has been done in the past in the matter of the permeation of metals by hydrogen, and also of the measure of success which has attended the attempt to free the gas from impurities by the method mentioned.

The fact of the permeability of hot platinum by hydrogen was first announced by Deville and Troost.[1] When hydrogen was introduced into a hot platinum tube surrounded by one

[1] Compt. rend., **56**, 977, (1863): Phil. Mag., [4], **26**, 336; Abstr., Jsb., 1863, 23; Chem. News, **7**, 294.

of porcelain filled with air, the former gas passed through the walls of the metal tube, but no passage of air into the inner tube could be detected. Later papers by the same authors[1] established the results claimed and showed that iron also was permeable by certain gases at high temperatures.

A year or two later Graham[2] repeated the experiments of Deville and Troost, taking, however, greater precautions to avoid error. His method differed in that, by means of a Sprengel pump, a vacuum was maintained within a platinum tube, which was closed at one end, and which was heated in an atmosphere of hydrogen. The gas was found to penetrate rapidly into the interior of the tube. When air was substituted for hydrogen, practically no gas was delivered by the pump, but Graham was of the opinion that air did penetrate to a slight extent. As however the connections of his apparatus were not above suspicion, and as he employed air which had been dried by sulphuric acid alone, the evidence for the penetration by air is by no means convincing. At the temperature employed, any water-vapor present in the air would probably have been at least partially dissociated and free hydrogen have been formed. The same objection might hold good for all his experiments in this series. When carbon dioxide was tried, 0.3 cc. of gas was collected by the pump and "an indeterminate small portion of this was condensed by baryta water and appeared to be carbonic acid." In view of the power of carbon dioxide to cling to the walls of a vacuous glass tube and to be but slowly removed, the evidence here, again, is inconclusive. Negative results were obtained with chlorine, hydrochloric acid gas, steam, and ammonia. When coal-gas containing hydrogen, methane, carbon monoxide and ethylene, was employed, hydrogen penetrated, but no evidence of carbon compounds could be obtained on exploding the gas collected with oxygen. Graham concluded that a little nitrogen might penetrate the platinum wall provided hydrogen was passing through at the same time

[1] (*a*) Compt. rend., **57**, 894, (1863); (*b*) *Ibid.*, **57**, 965; also Ann. Chem., (Liebig), **130**, 254; (*c*) Compt. rend., **59**, 102, (1864); Abstr. Jsb., 1864, 89; Phil. Mag., [4], **28**, 229; Chem. News, **10**, 57.

[2] Phil. Trans., **156**, 399, (1866); Phil. Mag., [4], **32**, 503; J. Chem. Soc., **20**, 257; Abstr. Proc. Roy. Soc., **15**, 223.

in the opposite direction, since he obtained evidence of such penetration when the tube was filled with hydrogen and heated in an atmosphere of nitrogen.

In accordance with conclusions arrived at by a study of the passage of gases through various septa, Graham assumed that the penetration of platinum by hydrogen was due to the liquefaction of the gas on the surface, the diffusion of the condensed gas through the material of the wall, and the evaporation of the liquid from the inner surface of the tube into the vacuum.

Nearly all research in this field since the publication of these results has had to do with the nature of the occluded gases, and not with questions of penetration considered by itself. Morse and Burton, however, have shown[1] that the hydrogen contained in the flame of an ordinary blast-lamp will penetrate a platinum vessel heated by that means; and Ramsay, in studying the phenomena connected with the passage of hydrogen through a palladium septum, has found[2] that this power was apparently possessed by no other gas examined. As palladium is permeable to a far higher degree than platinum, it would naturally be assumed that the latter metal would resist the passage of all gases except hydrogen completely.

In his studies of the properties possessed by hydrogen when occluded in platinum and palladium, Graham found that the metals could be more highly charged with the gas by making them serve as the negative pole of galvanic cells, than by heating them and allowing them to cool in an atmosphere of hydrogen.[3] "The occluded hydrogen," he says, "is certainly no longer a gas, whatever may be thought of its physical condition." Oxygen was not occluded when the current was reversed. The evidence, he considered, was on the whole against the view that chemical combination takes place between the metal and the gas. Careful examination of the change in volume suffered by palladium and its alloys on absorbing hydrogen led to the view that the gas was converted

[1] This JOURNAL, **10**, 148, (1888). It is to Professor Morse that I owe the suggestion of employing a platinum septum in this work.—W. W. R.

[2] Phil. Mag. [5]. **38**, 206, (1894).

[3] Proc. Roy. Soc., **16**, 422, (1868).

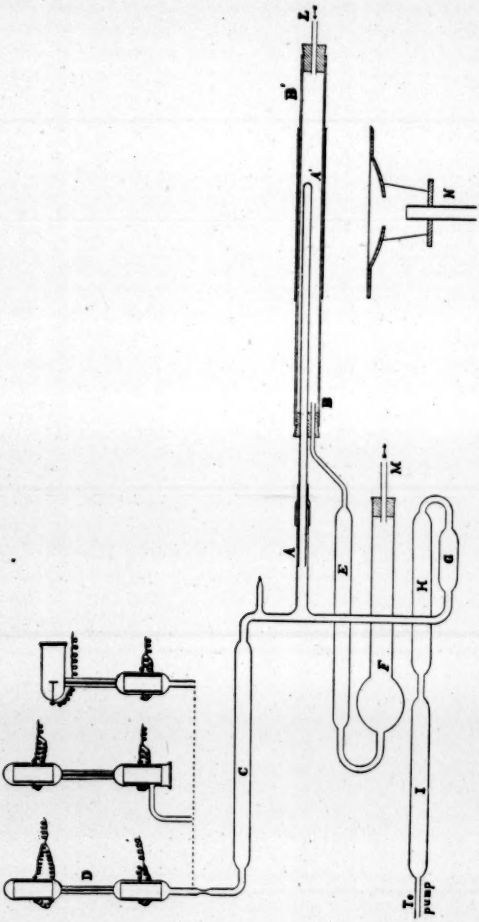
into a metal-like substance and formed a species of alloy with the palladium.[1] Hydrogen in this particular condition—"Hydrogenium," as Graham calls it—is magnetic, shows electric conductivity and possesses some tenacity. Its density varies: in palladium alloys it is 0.711–0.7545; in palladium itself, 0.854–0.872.

This conclusion was, however, challenged in the more recent work of Berthelot,[2] who as a result of thermochemical investigations, returned to the view that definite complex hydrides of palladium and platinum are formed. The results obtained by Thoma[3] had to do with the absorption of the gas considered as a case of solution capable of supersaturation. The conclusions of Berthelot have been offset by a research by Mond, Ramsay and Shields[4] upon platinum-black, in which doubt was cast upon the purity of the material used by the French chemist, and evidence given to show the untrustworthiness of his thermochemical data for establishing the condition of the occluded gas.

The method of spectroscopic examination seemed capable of yielding so much more accurate results in determining the presence of foreign gases in the filtered hydrogen than any of the analytical methods to my knowledge used hitherto in this work, that it seemed worth while to put it to trial. Tubes filled with gas were examined in the Physical Laboratory of this University, with the aid of a large concave grating specially prepared for such work, and photographs were made of each in turn. For their kindness in making these examinations, I am indebted to Dr. J. S. Ames and Mr. W. J. Humphreys.

The essential features of the apparatus used in the production of the gas to be tested are represented in the accompanying figure. It consists of a platinum tube, AA', about 350 mm. long, and of about 3 mm. internal diameter, closed at one end and sealed at the other, by means of fusible glass, into a soft-glass tube, which is in turn connected with the sparking-tube D and the Töpler pump. The closed end of

[1] Proc. Roy. Soc., **17**, 212, 500, (1869); Compt. rend., **68**, 1511.
[2] Compt. rend., **94**, 1377. (1882); Ann. chim. phys., [5], **30**, 519.
[3] Ztschr. phys. chem., **3**, 69, (1889).
[4] Phil. Trans., 186 A, 657, (1895); Abstr. Proc. Roy. Soc., **58**, 242.


L
B'
A'
N
B
M
A
E
H
G
F
C
I
To pump
D

the platinum tube projects into a piece of hard-glass tubing, BB', through which a current of dry gas, entering at L, could be passed, while at the same time the platinum tube can be heated by means of a Bunsen burner, N, below the combustion-tube. The latter is covered for a portion of its length with a layer of thick copper foil to distribute the heat, and with the aid of asbestos-board screens the temperature of the two tubes can be raised to a white heat. A plug of asbestos was pushed into the annular space between the two tubes to give support. A short piece of black rubber is drawn over the place where the platinum tube is sealed into the glass tube, is wired on and well shellaced, to guard against possible leakage from fracture.

The tube C is filled with phosphorus pentoxide. The gas entering at L has been made to pass through sulphuric acid, calcium chloride, soda-lime, and, finally, through a long tube filled with phosphorus pentoxide. It passes out at B through the guard-tubes E containing the pentoxide, and F containing calcium chloride and soda-lime. When hydrogen was the gas employed, it was first passed through four wash-bottles filled with acid, and two filled with alkaline permanganate solution, and then through a tube filled with red-hot copper turnings, on its way to the drying-tubes. It was hoped the latter device would free the gas from any admixture of oxygen, whether present as a constituent of air, or given off from the permanganate solution.[1]

The sparking-tubes were of several forms, at first with wire electrodes, afterwards with cylindrical electrodes of aluminium tubing or foil. In some cases photographs were made of the spectrum of the light emitted through the walls of the capillary tube; in others, of that observed "end on" through a disk of quartz sealed as a window to one of the bulbs. In one case the tube was specially constructed so that the light observed through the window was that produced at the electrode and not that in the capillary tube; the light thus obtained was, however, so weak that no photograph could be made of the spectrum.

Having demonstrated the tightness of the apparatus and the fact that at the temperature employed hydrogen is capa-

[1] See note 1, p. 691.

ble of permeating the walls of the platinum tube, experiments were made which afforded evidence that a similar power of penetration is not possessed by oxygen or nitrogen. Air was drawn through the apparatus while the metal tube was maintained at a white heat. Care was of course taken to have the air as dry as possible in order to avoid the presence of hydrogen through the dissociation of water-vapor. The vacuum within the metal tube could be maintained apparently indefinitely under these conditions.

The tubes were filled with hydrogen as follows: The carefully cleansed tube was sealed to the apparatus and, when the air had been completely exhausted, was left for twenty-four hours or more; by this time all moisture was probably removed by the phosphorus pentoxide. By continuous sparking and exhaustion the gas occluded by the electrodes was then removed, and a condition of brilliant green fluorescence readily obtained. On raising the mercury in the Töpler pump so as to compress all the gas in its bulb and tubes into a space of not more than a fraction of a cubic centimeter, and at the same time noting the change, if any, which took place in the height of the mercury column in the delivery-tube—in other words, on using the pump itself as a McLeod gauge—it could be shown that the pressure within the exhausted space was not more than one or two millionths of an atmosphere. Connection between the pump and the rest of the apparatus was then cut off by turning a glass tap, and hydrogen was admitted slowly into the sparking-tube by heating the metal tube while a current of dry purified gas was circulating about it. When the pressure inside the sparking-tube had reached about 1 cm., the heating was discontinued and the apparatus exhausted as before. The process of filling and exhausting was repeated from three to six times, after which the tube was filled to the desired pressure—which was between 3 and 8 mm.—and was sealed off. In some cases, as an extra precaution, the tube was enclosed in a copper air-bath and heated during the process of exhaustion to a temperature of 150°–200°, the sparking being meantime continued.

It may be as well to say that the passage of the hydrogen into the exhausted space was very slow as compared with

what the statements of Graham had led me to expect. It may be that the tube employed by me was thicker and more thoroughly hammered, and that the temperature obtained was not so high. At all events the pressure in the sparking-tube rose only at the rate of about a millimeter in three to five minutes, the volume of all the tubes and connections open to the gas being about 100 cc. On this account the time required to cleanse, exhaust, and fill the tube in the manner described, waiting in each case for diffusion to equalize the pressure throughout the long system of tubes, rendered the work very slow and tedious, especially as only a short time was available on any one day to be devoted to the work.

The sparking-tubes had at first, except for the tube *C*, been in direct connection with the Töpler pump and mercury gauges. On photographing the spectrum it was found that the gas was contaminated with the vapor of mercury. To avoid this difficulty the tubes *G*, *H*, and *I* were introduced between the pump and gauges and the system to be exhausted. *I* is a long tube filled with powdered sulphur, *H* a similar one containing bright copper turnings, and *G* contains gold-leaf. *H* and *I* are shown in the figure much shorter in proportion than they are in reality. So perfectly do these guard-tubes serve their purpose, that after one year the gold-leaf shows no signs of amalgamation. The copper has apparently held back all sulphur-vapors from the sparking-tubes, whereas the mercury in the manometers have become fouled from not being protected in its turn by copper. No trace of mercury-vapor has been detected in the gas contained in any of the sparking-tubes since the precautions mentioned were taken to exclude it.

Results.

A careful examination of the photographic negatives obtained when the hydrogen produced as described and contained in the sparking-tubes was used as the source of light, has failed to reveal the presence of any other substance—unless the so-called "compound" spectrum is to be considered an indication of such contamination. The purified hydrogen drawn through the combustion-tube *BB'* probably

frequently contained nitrogen, but no signs of that gas could be detected in the spectrum of what had passed into the inner tube. If the compound spectrum is due to the presence of water-vapor, it is not clear how it can be eliminated, no more efficacious drying agent than phosphorus pentoxide being available.

It may be well to mention here that the results obtained in the examination of the spectrum of hydrogen purified as described in this paper, do not seem to agree with those obtained by Messrs. Trowbridge and Richards.[1] According to these authors an oscillatory discharge from their powerful storage-battery through hydrogen did not yield the compound spectrum, whereas the direct discharge produced the compound spectrum as usual. In the experiments performed with hydrogen, as described in this paper, the discharge was that of a large Ruhmkorff coil, sometimes with and sometimes without a Leyden jar in the secondary circuit and with considerable variations of current in the primary coil. In no case was the compound spectrum absent. Messrs. Trowbridge and Richards do not mention the character of the tubes they employed, nor give any account of the method of purification used for the gas or that of cleansing and filling the tubes. It is just possible that were these data available, some explanation of the difference in our results might be forthcoming. It is true that the pressures used in this work were on the average a little higher than those employed by Trowbridge and Richards, but not to an extent, in all probability, sufficient to account for so marked a discrepancy.

As has been stated, oxygen and nitrogen do not penetrate hot platinum under the conditions described above; it remained an interesting question to determine whether this was due in any degree to the relatively high specific gravity of these gases as compared with hydrogen. Accordingly an experiment was made to see if marsh-gas, with a density only half that of oxygen, would penetrate into the inner tube. A large gasometer was filled with the gas prepared by heating a mixture of dehydrated sodium acetate and soda-lime, and washed with water and acid sodium sulphite solution to remove the vapors of ace-

[1] Am. J. Sci., [4], **3**, 118; Phil. Mag., [5], **43**, 137, (1897).

tone. After standing several weeks in contact with water in the gasometer, it was passed again through a solution of the sulphite, through soda-lime, calcium chloride, and sulphuric acid, to mix with the purified hydrogen as it entered the tube filled with hot copper turnings mentioned above.[1] After the air had been removed, and a gas-mixture, consisting of about four-fifths marsh-gas and one-fifth hydrogen, was being passed through the combustion-tube BB', the latter was heated. Gas passed very slowly into the sparking-tube; after about three hours the pressure had risen to only about 3 mm. Examination of the gas, by means of a large prism spectroscope, failed to show the presence of any carbon compound; but, on account of the low pressure, the light was too feeble to give any result with the photographic method, even after a very long exposure, and so this experiment will still require further and more accurate confirmation.

It is proposed to continue this work with hydrogen and other gases.

Since this paper was written, a note has been published by Ramsay and Travers,[2] in which they describe their attempts to pass helium and argon through septa of platinum, palladium, and iron, under conditions similar to those described in this paper. No evidence of such penetration was however obtained.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, June, 1897.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON SOME MALONIC ACID DERIVATIVES.

BY RICHARD S. CURTISS.

In their researches upon the haloid derivatives of ethyl malonate, Conrad and his students found that when ethyl chlormalonate was treated with cold concentrated alcoholic ammonia, the chlorine atom remained intact, the resulting crystalline compound being chlormalonamide, $ClHC<\begin{matrix}CONH_2\\CONH_2\end{matrix}$.[3] When, however, the reaction was continued for several hours

[1] It is not generally known that comparatively large quantities of oxygen are set free when hydrogen is made to bubble through potassium permanganate solution. Unless care is taken to remove this oxygen, say with red-hot copper and a drying agent, an opportunity is given for a very serious error in all experiments where pure hydrogen is desired. This reduction of permanganate by hydrogen is now under investigation in this laboratory by Prof. Morse.—W. W. R.

[2] Chem. News, 75, 253. [3] Conrad and Bischoff: Ann. Chem. (Liebig), 209, 231

at 140° in a sealed tube, a small yield of a compound was obtained,[1] apparently imidodimalonamide, $NH<^{CH<^{CONH_2}_{CONH_2}}_{CH<^{CONH_2}_{CONH_2}}$ along with some amidomalonamide, $NH_2—CH<^{CONH_2}_{CONH_2}$.

Ethyl chlormalonate, heated with boiling aniline for ten hours, gave a crystalline anilidomalonanilide,

$$C_6H_5NH—CH<^{CONHC_6H_5}_{CONHC_6H_5}.$$

Conrad and Brückner[2] obtained by the action of concentrated alcoholic solution of ammonia on ethyl dichlormalonate, at ordinary temperatures, dichlormalonamide, $Cl_2C<^{CONH_2}_{CONH_2}$, and dichloracetamide, while ethyl dibrommalonate treated with cold alcoholic ammonia, gave a small yield of an unstable body, doubtless, from the analysis, diamidomalonamide, and also some dibromacetamide. This diamidomalonamide, heated to 90°–100°, readily loses ammonia and gives a small amount of a substance which appears to be imidomalonamide, $NH=C<^{CONH_2}_{CONH_2}$.

In these experiments the ester seems to be converted into the amide before the haloid is substituted. On treating ethyl brommalonate with aniline, a weaker base than ammonia, one might expect an easy substitution of the bromine, without affecting the carbethoxyl group, with the formation of ethyl anilidomalonate, $C_6H_5NH—CH<^{CO_2C_2H_5}_{CO_2C_2H_5}$. Wishing to obtain this body and a knowledge of its properties for use in further research, this reaction has been carried out with satisfactory results.

The oxidation by mercuric oxide of ethyl anilidomalonate has led to the unexpected formation of ethyl dianilidomalonate, $\begin{matrix}C_6H_5NH\\C_6H_5NH\end{matrix}>C<^{CO_2C_2H_5}_{CO_2C_2H_5}$. I have also made this substance by the action of aniline on ethyl dibrommalonate, and have studied its properties.

[1] Conrad and Guthzeit: Ber. d. chem. Ges., **15**, 605. [2] *Ibid.*, **24**, 2994.

I have further investigated the behavior of sodium ethylate on ethyl dibrommalonate, with the view of forming ethyl diethoxymalonate, $\frac{C_2H_5O}{C_2H_5O}>C<\frac{CO_2C_2H_5}{CO_2C_2H_5}$, which, it was thought, would possibly lose alcohol on being treated with aniline and give ethyl phenylimidomalonate, $C_6H_5N=C<\frac{CO_2C_2H_5}{CO_2C_2H_5}$, by analogy with the behavior of the ketone ortho ethers toward aniline.[1]

Since the completion of my work in this line, a paper has appeared by Bischoff,[2] in which he announces the discovery of ethyl diethoxymalonate. I shall include the results of this part of my work, however, as they confirm his experiments and have been carried out somewhat more fully and under slightly different conditions.

The Action of Aniline upon Ethyl Brommalonate.

The ethyl brommalonate was prepared according to the method of Knoevenagel,[3] and the fraction boiling at 120°–122° under 14 mm. pressure, was used in the experiments. 49 grams of ethyl brommalonate were mixed with 56 grams (3 molecules) of aniline, and the mixture allowed to stand at ordinary temperatures. At first there was a slight evolution of heat. Aniline hydrobromide crystals soon formed, and in two hours the reaction was almost complete. After standing four days, the liquid was filtered off from the crystals, which weighed, after being washed with ether and dried, 32 grams (93 per cent. of the theoretical yield). The excess of aniline was removed from the ether solution of the filtrate by dilute hydrochloric acid, the ether dried over fused potassium carbonate and evaporated in a vacuum. The crystals which formed, washed with ligroïn, weighed 31 grams, and proved to be ethyl anilidomalonate. From the mother-liquor a small amount of the same body was obtained, together with a small amount of needle-like crystals, which melted at 117°–118°, and were ethyl dianilidomalonate, formed undoubtedly from a small amount of ethyl dibrommalonate,

[1] Claissen: Ber. d. chem. Ges., **29**, 2932. [2] *Ibid.*, **30**, 487; **29**, 1507.
[3] *Ibid.*, **21**, 1356.

which it was impossible thoroughly to separate from the monobrom derivative by fractional distillation.

The chief product was recrystallized from alcohol, dried in a vacuum over sulphuric acid, and on analysis:

0.2977 gram of the substance gave 0.6745 gram CO_2, and 0.1899 gram H_2O.

0.2820 gram of the substance gave 14.8 cc. N at 17°, and 746.8 mm.

	Theory for $C_6H_5NH-CH<^{CO_2C_2H_5}_{CO_2C_2H_5}$.	Found.
C	62.15	61.80
H	6.77	7.08
N	5.58	6.00

Ethyl anilidomalonate crystallizes from alcohol or ligroïn in crystals 2 cm. or more long, which belong to the monoclinic system; it has a greenish-white tint, a bitter taste, melts at 44°–45° to a clear liquid, is easily soluble in carbon disulphide, alcohol, ether, benzene, and chloroform; fairly soluble in ligroïn (boiling-point 70°–80°), insoluble in water and dilute hydrochloric acid, and soluble in potassium hydrate solution. It decomposes on heating, turns dark, and gives off an odor similar to that of an isonitrile. Dry hydrochloric acid gas gives, in an ethereal solution of the body, a colorless crystalline compound, soluble in much ether. In alcoholic solution with alcoholic sodium ethylate, at ordinary temperatures, a sodium salt is precipitated. One molecule of bromine in a chloroform solution of the ester gives fine silky white needles with little loss of hydrobromic acid.

Pure ethyl anilidomalonate reduces an ammoniacal silver nitrate solution very strongly, even in the cold, and is easily oxidized by mercuric oxide when heated.

Oxidation of Ethyl Anilidomalonate by Mercuric Oxide.

Six grams of ethyl anilidomalonate in 10 cc. of ligroïn (boiling-point 100°–110°), together with 8 grams of freshly precipitated dry mercuric oxide, were heated for three hours at 95°–100°, in a flask with a reverse condenser. Much metallic mercury separated out. The liquid, filtered from the mercury salt and evaporated in a vacuum, gave five grams of a green oil, from

which 2.5 grams of a crystal compound were obtained. This, purified by boiling in alcoholic solution with bone-charcoal and recrystallized from alcohol, gave rosettes of white, silky needles, melting at 117°–118°. On analysis this body proved to be ethyl dianilidomalonate instead of the expected ethyl phenylimidomalonate. The study of this peculiar reaction will therefore be continued.

0.2735 gram substance gave 0.6652 gram CO_2, and 0.1596 gram H_2O.

	Theory for $(C_6H_5NH)_2>C<(CO_2C_2H_5)_2$.	Found.
C	66.66	66.33
H	6.43	6.48
N	8.19	....

The Action of Aniline upon Ethyl Dibrommalonate.

The ethyl dibrommalonate was made according to the method of Conrad and Brückner,[1] and the fraction boiling at 142°–143°, under 18 mm. pressure, was used in these experiments.

19 grams of the ethyl dibrommalonate were mixed with 28 grams of aniline (5 molecules). There was no perceptible evolution of heat, but aniline hydrobromide soon began to separate out. After allowing the mixture to stand at 50°–60° for six days, it was extracted with ether, leaving 18 grams of aniline hydrobromide, or 85 per cent. of the theoretical yield. The ethereal filtrate evaporated on the water-bath gave 10.5 grams of impure crystals which, after filtering on the pump, are best freed from the adhering oil by spreading on a clay plate.

Purified by recrystallizing from 60 per cent. alcohol, after boiling with bone-charcoal, the body melts at 117°–118°, and distils with little decomposition. It crystallizes from absolute alcohol in rosettes of long, colorless, silky needles, easily electrified by rubbing. It is easily soluble in ether, acetone, aniline, carbon tetrachloride, and acetic ether; fairly so in alcohol, and difficultly soluble in ligroïn. It dissolves in concentrated hydrochloric acid, is not readily saponified by aqueous potash; but sodium alcoholate gives an immediate precipitate of sodium salt from an alcohol solution.

[1] Ber. d. chem. Ges., 24, 3001.

Purified as above, dried in a vacuum over sulphuric acid and analyzed, it gives the following results:

0.2345 gram of the substance gave 0.5730 gram CO_2, and 0.1380 gram H_2O.

0.2347 gram of the substance gave 17.2 cc. N at 23°, and 733.5 mm.

	Theory for $(C_6H_5NH)_2>C<(CO_2C_2H_5)_2$.	Found.
C	66.66	66.64
H	6.43	6.54
N	8.19	7.97

This body is not oxidized by mercuric oxide or ammoniacal silver nitrate solution, and is identical in every respect with the product obtained by the oxidation of ethyl anilidomalonate described above. It can be heated for an hour in sealed tubes at 100°–120°, with little apparent change. Heating with aniline at temperatures ranging from 100°–200°, in sealed tubes, with the idea of forming dianilidomalonanilide, gave no satisfactory results.

The Action of Sodium Ethylate on Ethyl Dibrommalonate.

The interaction between ethyl dibrommalonate and alcoholic sodium ethylate under various conditions, such as temperature; an excess of one or the other reagent; mode of mixing was found to give in all cases a complicated mixture of compounds. Ethyl diethoxymalonate, $\begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}>C<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$, which it was expected would be the chief product of the reaction, was obtained in largest amount when the following conditions were present: 95.8 grams of ethyl dibrommalonate in 30 cc. of absolute alcohol were dropped, by means of a separating funnel, into 225 cc. of absolute alcohol, in which 13.8 grams (2 atoms) of sodium had been dissolved. The temperature was kept at 48°–50° by the heat of the reaction, and a small amount of carbon dioxide gas was continuously evolved. When all the ethyl dibrommalonate had been added the mixture was allowed to stand for one hour at 60°. The contents of the flask then consisted of a large amount of light-colored sodium salts covered by a straw-colored alcoholic liquid.

The alcohol was distilled off in a vacuum at 27° and 35 mm.

pressure. This distillate contains a small amount of a bromine body, and gives, when boiled with aniline and caustic potash, a strong odor of phenyl isocyanide, indicating the presence of bromated methane derivatives (Bromoform?). The presence of some one of these derivatives is very noticeable when sodium methylate is used in place of sodium ethylate, when there is a very strong and unmistakable smell like bromoform in the flask during the reaction. Boiled down with ammoniacal silver nitrate solution, the distillate gives a silver mirror (aldehyde?), and smells of ethyl carbonate.

After distilling off the main part of the alcohol, the residual red oil, filtered from 54 grams of sodium salts (A) and diluted with 6–8 volumes of ether, gave 14.7 grams more salt (B). An additional 3 grams of salt (C) were obtained by washing the ethereal filtrate from B with a few cc. of water, making a total yield of 71.7 grams (21.7 grams in excess of the theoretical amount of sodium bromide). As this salt contains much carbonate, and the latter fractions (B and C) a considerable amount of a sodium salt of an oily organic acid, the reaction is evidently a very complex one.

The ether solution, thus freed of all inorganic bodies, dried with potassium carbonate, and evaporated in a vacuum, leaves 24 grams of a fragrant red oil. Distilled in a vacuum it gives:

Fraction I.—4 grams of a fragrant, colorless, refractive oil boiling at 46°–48° under 18 mm. pressure. (An analysis is given below).

Fraction II.—0.5 gram, boiling-point 90°–127°, under 18 mm. pressure.

Fraction III.—2 grams, boiling-point 127°–138°, under 18–16 mm. pressure.

Fraction IV.—13 grams of a thick, colorless oil, distilling at 143°–146° under 16 mm. pressure. In the flask 2.8 grams of a red oil remained.

From Fractions III. and IV. 11 grams of colorless crystals were obtained, which proved to be ethyl diethoxymalonate. These recrystallized from absolute alcohol melt at 43°–44°. (Bischoff 43°–44°). Dried in a vacuum over sulphuric acid and analyzed, they gave the following results:

0.2488 gram of the substance gave 0.4829 gram CO_2, and 0.1811 gram H_2O.

	Theory for $\frac{C_2H_5O}{C_2H_5O}>C<\frac{CO_2C_2H_5}{CO_2C_2H_5}$.	Found.
C	53.23	52.94
H	8.07	8.08

Ethyl diethoxymalonate is a thick, colorless oil, crystallizing on cooling in prisms of the orthorhombic system. The crystals melt at 43°–44°, and distil with little decomposition above 225°. From a saturated alcoholic solution beautiful, transparent plates 3–4 cm. square may be obtained. It is very soluble in alcohol, benzene, chloroform, carbon tetrachloride, acetone and aniline, and difficultly so in ligroïn. The body reduces ammoniacal silver nitrate on long boiling in alcoholic solution, while cold alcoholic sodium ethylate precipitates a white sodium salt. Heated with aniline in sealed tubes at various temperatures up to 270°, it gave no satisfactory results, while some unchanged ester was recovered. It is, therefore, under these conditions, much more stable than the keto ortho esters studied by Claissen.

Fraction I. was redistilled for the third time between 127°–129° at ordinary pressure, and on analysis:

0.1896 gram of the substance gave 0.3428 gram CO_2, and 0.1477 gram H_2O.

	Theory for ethyl carbonate. $(C_2H_5O)_2>CO$.	Found.
C	50.84	49.9
H	8.47	8.6

The low value obtained for carbon is due to the presence of a trace of bromine product, which cannot be removed by repeated distillations. The characteristic odor, boiling-point, analysis, and general properties, leave no doubt, however, that the product is ethyl carbonate (boiling-point, 126°).

36 grams of sodium salt from the above experiment (including all the fractions B and C), shaken with dilute sulphuric acid and ether, gave 8 grams of an oil having a strong smell like acetaldehyde, and reducing ammoniacal silver solution even in the cold. Heated it loses much carbon dioxide at 180°–190°.

A second experiment with ethyl dibrommalonate and sodium ethylate, carried out like the first, except that the reaction-temperature was 10°–15°, gave 65 grams of sodium salts. The amount of carbonate in this salt was apparently much less, and no evolution of free carbon dioxide gas occurred. The ethereal solution gave 16.2 grams of oil, 2.4 grams of which distilled off between 120°–130° at ordinary pressure, and was chiefly ethyl carbonate. The residual oil in the flask gave 4.5 grams of ethyl diethoxymalonate on standing.

A third experiment was made, the conditions of the reaction being the same as in the first, except that 4 atoms of sodium (27.68 grams) were used instead of two, and the temperature was kept at 70°–75°, with a final heating of the flask for ten minutes at 100°. 73 grams of sodium salts containing much carbonate were then separated, and the rest (quantity not determined) finally removed by washing with dilute sulphuric acid and water. The ethereal solution then evaporated on the water-bath gave 19.2 grams of a thin red oil. On distillation 5–6 grams of a low-boiling oil (35°–38° under 47–18 mm.), mostly ethyl carbonate, were obtained. It had, however, a strong aldehyde odor, and reduced ammoniacal silver nitrate solution on warming.

9.6 grams of thick red oil remained in the distilling flask. This gave, on standing for a week at 0°, no sign of ethyl diethoxymalonate crystals.

The effect of reversing the mixing process and dropping the sodium ethylate into the ethyl dibrommalonate, is shown in the following experiment: The temperature of the reaction was 30°–40°, the other conditions being the same as the first experiment. As the addition of sodium ethylate took place bubbles of carbon dioxide gas arose. 57.6 grams of sodium salt were obtained. The ether filtrate evaporated on the water-bath left a fragrant oil, from which, on standing, 5 grams of colorless prismatic crystals of the monoclinic system were obtained. Recrystallized from 70°–80° ligroïn and dried in a vacuum over sulphuric acid, it melted at 56°–57°. The analyses, together with its general properties, prove that it is acetylene-tetracarboxylic ethyl ester.

0.1908 gram of the substance gave 0.3728 gram CO_2, and 0.1085 gram H_2O.

	Theory for $(C_2H_5O_2C)_2>C=C<(CO_2C_2H_5)_2$.	Found.
C	53.16	53.29
H	6.33	6.31

The mother-liquor from these crystals distilled at ordinary pressure gave 2 cc. of an oil (boiling-point, 122°–127°), which was chiefly ethyl carbonate. When the temperature of the distilling bath was raised to 280°, no trace of ethyl diethoxymalonate passed over, neither could any crystals of the same be found in the residual brown oil, on standing.

The following table gives a brief summary of the above four experiments:

Experiment.	1.	2.	3.	4.
Temperature	48°–50°	10°–15°	70°–75°	32°–40°
Atoms of sodium used	2	2	4	2
Sodium salts	71.7 gr.	65	73+	57.6
Carbonate present	much	much less than Exp. 1.	large amount	much
Free CO_2 gas	little	none.	large amount	little
Ethyl carbonate	4 gr.	2.4	5–6	2
Crude oil	24	16.2	19.2	not weighed
Ethyl diethoxymalonate	11	4.5	none	none
Acetylenetetracarboxylic ethyl ester	none	none	none	5 grams

Since the appearance of Bischoff's paper on the action of sodium ethylate on ethyl dibrommalonate, I have discontinued the studies along this line. I have shown, however, that operating under more favorable conditions, the yield of ethyl diethoxymalonate is much larger than he obtained. From 95.8 grams ethyl dibrommalonate he obtained 5.9 grams of oil boiling within 20°, *i. e.*, from 240°–260°, but gives no yield of pure crystals, while my yield from the same amount of substance is 15 grams of oil boiling between 127°–146° under 16

mm., yielding 11 grams of pure crystals. I mention this as he explains his low yield on the ground of "unfavorable dynamical conditions." Bischoff makes no statement concerning the formation of ethyl carbonate, free carbon dioxide gas, acetylenetetracarboxylic ethyl ester, or bromated methane derivatives in the reaction.

The fact that acetylenetetracarboxylic ethyl ester is formed by the addition of alcoholic sodium ethylate to ethyl dibrommalonate (Experiment 4) is of interest: it shows that sodium ethylate is capable of removing the bromine from this compound just as Conrad and Brückner[1] have shown is the case on using metallic sodium in benzene solution.

The formation of considerable amounts of free carbon dioxide gas, sodium carbonate and ethyl carbonate (to the largest extent in Experiment 3, temperature 75°, and least in Experiment 2, temperature 10°–15°), shows the easy splitting off of the carboxyl groups. The undoubted presence of bromated methane derivatives would indicate that the loss of carboxyl takes place, at least in part, before the withdrawal of bromine occurs. This peculiar behavior seems analogous to the formation of bromoform by the action of calcium hydroxide or caustic potash solution on dibrommalonamide, as noted by Freund,[2] and the formation of the same body when dibrombarbituric acid is treated with a warm solution of barium hydroxide.[3] The formation of acid oils indicates a saponification of the esters by sodium ethylate, producing sodium salts.

I shall continue experiments, already under way, upon the action of aniline on dibrommalonic acid, mesoxalic ester and acid, and also study further the properties of ethyl dianilidomalonate.

CHICAGO, MAY, 1897.

[1] Ber. d. chem. Ges., **24**, 3004.
[2] *Ibid.*, **17**, 783.
[3] Baeyer: Ann. Chem. (Liebig), **130**, 134.

THE ACTION OF NITRIC ACID ON TRIPHENYLMETHANE.

By E. S. Smith.

The method of preparing trinitrotriphenylmethane by the action of fuming nitric acid on triphenylmethane, is described by Fischer.[1] In an attempt to make this preparation I departed from the exact directions of Fischer and obtained a substance shown by analysis to be triphenylcarbinol, $C.OH.(C_6H_5)_3$. Following are the details of the work: I placed in a flask an unweighed quantity of triphenylmethane recently crystallized from benzene, and probably still retaining a little benzene; poured in an unmeasured quantity of nitric acid (sp. gr. 1.34), and then some fuming nitric acid; allowed the mixture to stand a short time, then heated on the sand-bath for a few minutes. After the reaction was ended a large amount of water was poured in. The reddish-yellow precipitate formed was filtered off on a platinum cone. By pressing down the precipitate a small amount of a red oil, having the smell of nitrobenzene, was forced out. The solid substance was purified by treating it with hot glacial acetic acid, crystallizing it from a mixture of benzene and glacial acetic acid, recrystallizing from benzene, and finally from alcohol. The purified substance is white, resembles triphenylcarbinol, and melts sharply at 161° (uncorr.). A test for nitrogen by the Prussian-blue method, showed absence of nitrogen.

0.138 gram gave 0.0773 gram water, and 0.4458 gram carbon dioxide, indicating the following composition:

	Calculated for triphenylcarbinol.	Found.
C_{19}	87.80	88.10
H_{16}	6.15	6.22
O	6.15	....
	100.00	

Several attempts to confirm this work by repeating it were, on the whole, unsuccessful, though various modifications in the strength of acid, manner of heating, etc., were tried. In one case a very small quantity of a white crystalline substance

[1] Ann. Chem. (Liebig), 194, 254.

was obtained which, after recrystallizing from benzene, melted at 161°.

Nitric acid of sp. gr. 1.42 does not act upon triphenylmethane until the temperature is raised to about 100°; but the product obtained in this case, as in most of the other experiments, was a waxy substance of salmon color, from which I was not able to get a crystalline compound.

I could find no record of triphenylcarbinol having been made in this manner; the usual method of preparation is to oxidize the triphenylmethane with chromic acid.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
BALTIMORE, JUNE, 1897.

REVIEWS.

DAS STUDIUM DER TECHNISCHEN CHEMIE AN DEN UNIVERSITÄTEN UND TECHNISCHEN HOCHSCHULEN DEUTSCHLANDS UND DAS CHEMIKER-EXAMEN. VON PROF. DR. FERD. FISCHER. Braunschweig: Friedrich Vieweg und Sohn. 1897.

In the preface to this short but interesting book, attention is drawn to the fact that there are in Germany but about 200 professional chemists who pursue their studies with a purely scientific aim, while there are about 4000 who devote themselves technically to the various forms of chemical industry. It is to the training of the latter class, 95 per cent. of the whole, —and in Germany only (the Austrian Empire and Switzerland not being included)—that consideration is given by the author.

The marked prominence of the position which Germany has taken in chemical manufactures during the latter half of this century, has attracted great attention in Europe, and is widely recognized on this side of the Atlantic, so that a discussion by so well informed an authority as Prof. Ferd. Fischer of the education of German technical chemists, is well worth reading.

He treats historically of the teaching of chemistry at the German universities, assigning the position of the earliest teacher of chemistry to J. Hartmann, at Marburg, in the early part of the 17th Century, and claiming for Göttingen in the middle and latter part of the 18th Century the first public recognition of chemical technology among university studies. Then is presented a list of the courses now (1895–6) given in chemical technology in the various German universities. Then follows an extended account of the courses of this kind offered at the special polytechnic schools of Germany, and the

tests of progress demanded of their students. Next comes a long list of the firms and individuals engaged in the various branches of chemical industry throughout the country, with the dates at which they began work, presenting a striking picture of the development attained within a comparatively short period of the recent past. Such a statement as this—that the *Farbenfabriken, vorm. Fr. Bayer & Co.*, in Elberfeld, which, in 1881, employed fifteen chemists and 500 workmen, and in 1896 had 104 chemists and 2644 workmen—justifies the author's exclamation, "*Wahrlich, ein glänzender Aufschwung!*" There is then a lengthy discussion of the desirability of a public, governmental examination for technical chemists, by which their fitness for employment may be tested. This involves consideration of the nature of the preparation which should be aimed at.

The main ideas suggested throughout are, 1st, that the only solid foundation for successful industrial chemistry is a thorough study of chemistry as a science. The author says emphatically: "Die hohe Entwickelung der chemischen Industrie Deutschlands *lediglich dem umfassenden Wissen und Können der deutschen Chemiker zu danken ist.* . . . Nicht *Handarbeit*, sondern *angestrengteste Geistesarbeit* ist hier entscheidend." 2d, that on this must be based, and to this must be added, an extended study of the special conditions involved in profitable work upon the large scale, of the practically available sources of raw materials, of the construction and use of specially devised machinery, of possible channels for the utilization of by-products, of questions of transportation and of markets, of the indirect consequences of changes taking place in any one line of industry, and many other matters which need to be kept in view and seen in their mutual relations, by the man whose education has been that of the true chemist, but is not that of the chemist only. J. W. M.

WATER AND PUBLIC HEALTH: the Relative Purity of Waters from Different Sources. By JAMES H. FUERTES, Member of the American Society of Civil Engineers. New York: John Wiley & Sons. London: Chapman & Hall, limited. 1897.

This little book, of seventy-five pages, aims at a discussion of the character of the water supply, the death-rate from typhoid fever, and the relation of cause and effect between these two, for a number of the larger cities of the world, chiefly in Europe and the United States. Statistics are quoted which have undoubted interest, but the work hardly deserves much praise for the use made of these. There is a lack of clearness. This is partly due to defects in the English employed, as, for example, in the sentence on p. 28, "usually the effect

of sedimentation and oxidation have been largely overestimated." But the logic, as well as the grammar, may without unfairness be unfavorably criticised: thus, on pp. 22 and 23, the opening sentence of a chapter reads: "If the drinking water supplied to cities is an index of their healthfulness, as measured by the typhoid fever death-rates, we should expect to find some sort of relation existing between the quality of the water and the typhoid death-rates." Exceptions might well be taken to some of the statements as to the sources of water supply of certain cities named, as, for instance, Paris, France, and New Orleans, La. There is no doubt whatever as to the soundness of the general conclusion, that the use of drinking water polluted by decaying organic matter, is habitually accompanied or followed by a high death-rate from typhoid fever. But the author's classification, under eight heads, of special sources of water supply, and the different rates of mortality from typhoid disease which he tries to connect with these, seems much less well established, in view partly of the great complexity of the conditions involved, and partly of the range of variation in each of the classes discussed. A point worth noticing is the apparent greater or less extent of mortality from typhoid fever in certain of the years for which tables are given, irrespective of the localities, and applying alike to widely separated European and American cities. J. W. M.

FRÜHLING UND SCHULZ' Anleitung zur Untersuchung der für die Zucker-Industrie in Betracht kommenden Rohmaterialien, Producte, Nebenproducte und Hülfs-substanzen. 5te, umgearbeitete und vermehrte Auflage, herausgegeben von DR. R. FRÜHLING. Braunschweig: Friedrich Vieweg und Sohn. 1897.

A good example of the full, well arranged, and clearly written manual of the pains-taking German expert in a special field of industrial chemistry. Appearing first some twenty years ago, this work has been carefully worked over in each succeeding edition, until now the fifth is published with judicious omission of matter that has become obsolete, more complete development of what has been retained, and introduction of no small amount of that which is entirely new and valuable.

The chief divisions of the book are the following: The sugars and materials containing sugars, which are of manufacturing interest, including the chemical and physical methods for their examination and quantitative determination; animal charcoal; water; limestone and lime as used in the sugar industry; strontianite and other compounds of strontium; gas (carbon dioxide) used for precipitation; soda

and hydrochloric acid used in the treatment of animal charcoal; fuel and fuel gases; *vinasse* from the distillation of molasses spirit; cattle food involving the use of molasses in its preparation; fertilizers and the materials for their manufacture, etc.

As respects intermediate and secondary products, it is the beet sugar industry which has been chiefly kept in view.

There are clear and good engravings in illustration of apparatus and its application, a detailed chapter on reagents and reagent solutions, and a series of twenty-seven useful tables, several of them specially relating to matters connected with the sugar industry. To any one interested in this branch of manufacturing chemistry, the book will be welcome and valuable. J. W. M.

TABELLARISCHE UEBERSICHT DER PYRAZOLDERIVATE. VON DR. GEORG COHN. Braunschweig: Viewig. 1897. pp. 443.

The pyrazol derivatives, of which antipyrine is the best known, have been the subject of a very large number of investigations, and the material accumulated is embarrassingly abundant. The author of this book has brought together all of this material in tabular form, and his work will undoubtedly be of value to those who may have to deal with the compounds of this group. The author says that foreign publications have been treated indirectly through the abstracts found in German journals. That is not a scholarly way of treating them, to say the least.

THE CHLORINATION PROCESS. BY E. B. WILSON, E.M. New York: John Wiley & Sons. London: Chapman & Hall, Limited. 1897. pp. 125. Price, $1.50.

This is a brief, clear account of the chlorination process for treating gold ores. The author claims for the method that "while old, yet it is new;" and that "it has assumed a place in metallurgy from which it cannot be dislodged." Chemists who have not been specially occupied in the field of metallurgy, will find this book interesting and instructive.

TABELLEN FÜR GASANALYSEN, GASVOLUMETRISCHE ANALYSEN, STICKSTOFFBESTIMMUNGEN, etc. VON PROF. DR. G. LUNGE. Braunschweig: Vieweg. 1897.

The well-known tables of Lunge have been prepared in a form adapted to use as charts, the type being large and clear. In this form they will no doubt prove of value to every laboratory.